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METHODS OF QUANTITATIVE ORGANIC ANALYSIS

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METHODS OF QUANTITATIVE ORGANIC ANALYSIS

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METHODS

OF

QUANTITATIVE ORGANIC ANALYSIS

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BY

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AND

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WITH DIAGRAMS

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INTRODUCTION.

The student taking up quantitative organic analysis will find at the outset how greatly it differs from the corresponding work in inorganic chemistry. The methods employed in the latter are so much simpler, more rapid, and above all, so much more capable of giving accurate results. They are essentially based on ionic reactions in which the time factor scarcely enters at all and they admit of exhaustive systematic generalization; thus, all soluble chlorides can be estimated by precipitation with silver nitrate, soluble sulphates by precipitation with barium chloride, and so on. With due care such processes admit of very accurate results. It is different in the case of organic substances, where the ionic theory has little if any application, and reactions are governed by a whole series of factors of which time is by far the most important.

The influence of time is one which must never be overlooked even in what may appear to be the simplest of reactions. It pervades almost every type of chemical interchange—hydrolysis, oxidation, reduction and the formation of condensation products. In many cases the methods of analysis themselves have been utilized for the study of the relative activities of allied compounds, and of such it suffices to

mention the researches of Stewart and of Petrenko-Kritschenko on the carbonyl group, and of Remsen and Reid on the hydrolysis of acid amides. It is obviously impossible to estimate aldehydes and ketones, e.g. by the method of Watson-Smith, unless it is certain that complete hydrazone formation has been attained, and this is largely a question of time.

Of the other factors which play a great part in quantitative organic work, temperature comes next in importance. It is fortunate that in general a rise in temperature increases the velocity of reaction, as otherwise an analysis would be a tediously long undertaking.

It must further be kept in mind that the simple equations to which one has become accustomed in the theoretical study of the subject seldom represent the whole of the facts. In qualitative work it is sufficient to know the main course of the reaction between the substances employed and to leave other possibilities out of consideration. In quantitative work it is necessary to so adjust time, temperature, concentration and other factors so as either to avoid altogether, or reduce to an absolute minimum, the possibility of the reaction taking, in any degree, a course other than that desired.

Many reactions in general use are empirical in character; that is to say, their course cannot be represented accurately by any single chemical equation. This is especially so in the reduction of Fehling's solution by carbohydrates or by phenylhydrazine. In such cases it is necessary to put on a blank, working as nearly as possible under the same conditions and using pure material. Whenever possible such blank

experiments are made, since they compensate the actual determinations for disturbing influences which cannot be avoided or allowed for by calculation.

Having obtained the conditions for the accurate estimation of one substance, it is interesting to test these on an allied compound; for example, to endeavour to determine acetaldehyde by the bisulphite method under the same conditions which have been found best for formaldehyde. In nine cases out of ten the result will prove more or less disappointing. General methods of analysis are not readily attainable in organic chemistry, and this is largely due to the predominance of spacial influences among organic bodies compared with the commoner inorganic bodies. It has therefore become necessary to take one compound at a time and investigate thoroughly the conditions of the methods for its exact analysis. In many cases such work is of great difficulty as systematic examination of original literature shows. One of the hardest problems is the separation of one organic substance wholly and quantitatively from others with which it may be associated. Ethyl alcohol provides an excellent example of this. The number of methods proposed for its estimation in commonly occurring mixtures is very large, and the cause of this is that up till the present there is no generally convincing, satisfactory procedure by which this apparently simple problem may be solved. As a general rule the greater the volume of literature concerning an analytical problem, the greater is the unreliability, or restricted application, of the methods proposed.

The arrangement we have considered advisable is

to divide the subject-matter on general quantitative organic analysis into two separate parts. One of these is capable of some little generalization ; the other deals with each substance individually. Chapter III is therefore devoted to a study of the commoner methods employed in the estimation of typical groups, based on characteristic qualitative reactions, such as, e.g. the reduction of nitro groups in acid solution to amino groups. Even in the most general estimations it is desirable for the reasons above given to cite, where possible, the results got for particular compounds belonging to the general class under consideration.

In this direction we suggest that most useful investigations might be carried out on the application of general methods of analysis to a group of allied substances. This has recently been accomplished by Feinberg in the case of aldehydes, and a short summary of his paper has been included in the discussion of that group. The results he has obtained are of such importance as to lead one to expect that an extension of the work to other classes of compounds would provide very valuable information. The methods in Chapter III are not meant to be applied indiscriminately to any individual substance of the general class, but rather to serve as a basis for a little research into the conditions under which such methods are applicable to its exact estimation.

The second division of the subject comprises some organic bodies of technical as well as purely scientific importance. In the last chapter are brought together the standard methods for the analysis of a few of these, wherever possible giving results based on a

comparative study of the principal methods in use for the particular compound. A thorough research into the relative value of several methods proposed for one compound gives a greater insight into the work than a few determinations chosen indiscriminately. It is hoped that the collection of substances included is such as to give the student a general idea of some technical estimations.

The importance of molecular weight determinations, especially from the purely scientific standpoint, and of ultimate analysis in both pure and applied chemistry, is such as to need no comment on their inclusion. In Chapter II the well-tried methods are given, together with those modifications for shortening the time of analysis that have stood the test of experience.

The arrangement adopted in this work is based on a series of six lectures, which we attended as students during the session 1911-1912, given by Dr. M. A. Whiteley, at the Imperial College of Science and Technology, London. We are especially indebted to Dr. Whiteley for her kindness in placing her unique set of references at our disposal, this forming a nucleus for a systematic study of the Scientific Journals. We wish to add that descriptions of processes modified by Dr. Whiteley are to be found on

Page 42, lines 1-2 from bottom
„ 83, „ 7-14 „ „ and figure
„ 86, „ 1-3 „ „
„ 229, „ 1-2 „ „ and figure.

Other acknowledgments are to be found in the text. We have made use of the Abstracts of the

Chemical Society, but the great majority of the references have been confirmed. We are greatly indebted to Mr. Stanley Robson, M.Sc., for reading through our manuscript, and for valuable suggestions; also to our publishers for their kindness in permitting changes while the book was in the press.

P. C. R. KINGSCOTT.
R. S. G. KNIGHT.

London, 1914.

CONTENTS.

PAGE

Introduction v

International Atomic Weights, 1914 xiii

Abbreviations xv

CHAPTER I.

The Determination of Molecular Weight by Physical Methods 1

CHAPTER II.

Ultimate Analysis 23

CHAPTER III.

Estimation of Typical Groups 69

CHAPTER IV.

Estimation of Some Compounds of Technical Importance . . 133

Name Index 277

Subject Index 281

1914.

International Atomic Weights.[1]

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

[1] Journ. Chem. Soc. London.

ABBREVIATIONS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Ann.	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal. appl.	Annales de Chimie analytique appliquée à l'Industrie à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Arch. Pharm.	Archiv der Pharmazie.
Atti Lincei	Atti della Reale Accademia dei Lincei Rendiconti.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Bioch. Zeit.	Biochemische Zeitschrift.
Bull. assoc. chim. sucr. dist.	Bulletin de l'association des chimistes de sucrerie et de distillerie de France et des Colonies.
Bull. soc. chim.	Bulletin de la société chimique de France.
Bull. U.S. Bur. Chem.	Bulletin of the U.S. Bureau of Chemistry.
Chem. News	Chemical News.
Ch. Rev.	Chemische Revue.
Chem. Rev. Fett- u. Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit / Chem. Ztg.	Chemiker Zeitung (Cöthen).
Chem. Cent. / Chem. Zent.	Chemisches Zentralblatt.
Comp. rend.	Comptes rendus de l'Académie des Sciences.
Dingl. Poly. J.	Dingler's Polytechnisches Journal.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahresberichte	Jahresberichte der Chemie (Berzelius).
J. Am. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry.
J.C.S. { Trans. / Abst. / Proc. }	Journal of the Chemical Society { Transactions. / Abstracts. / Proceedings. }
J. für Land.	Journal für Landwirtschaft.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Land V-St.	Landwirtschaftliche Veruchs-Stationen.
Monats.	Monatschefte für Chemie.

M.u.J.	Lehrbuch der organischen Chemie von V. Meyer und P. Jacobson.
Mon. Sci.	Moniteur Scientifique.
Öst. Ch. Ztg.	Chemiker Zeitung, österreichische.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zent. / Pharm. Cent.	Pharmazeutische Zentralblatt.
Proc. A.O.A.C.	Proceedings of the Association of Official Agricultural Chemists.
Rec. trav. chim.	Receuil des travaux chimiques des Pays Bas et de la Belgique.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Farb.	Zeitschrift für Farbenindustrie.
Zeit. Nahr. und Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. physiol.	Zeitschrift für physiologische Chemie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutsche Zuckerindustrie.
Zeit. Zuck.	Zeitschrift für Zuckerindustrie in Böhmen.

CHAPTER I.

THE DETERMINATION OF MOLECULAR WEIGHT BY PHYSICAL METHODS.

A knowledge of the molecular weight of a compound is of the greatest importance. Once it is known many other exact properties of the substance can be often readily obtained by simple processes. In the case of acids and bases, for example, direct titration against standard alkali and acid enables one immediately to calculate the basicity or acidity of the substance, thus giving a ready method of quantitatively analysing solutions of these.

Physical methods of determining molecular weight are never highly accurate. The numbers so obtained, however, serve to show the relation between the molecular weight and the empirical formula weight. The latter is capable of very exact measurement by the methods of ultimate analysis given in Chapter II. Physical determinations show immediately the integer by which the formula weight must be multiplied in order to arrive at the exact molecular weight.

The methods given in this chapter may be divided into two sets, viz. determinations of the molecular weight of the substance in the form of vapour, and of the substance in solution.

In interpreting the results of experiments it must be carefully borne in mind that disturbing factors may arise which vitiate the conclusions ordinarily arrived at. Many organic substances on vaporization decompose, or perhaps dissociate into other forms, rendering the vapour density determinations too low, or as in the case of acetic acid simple molecules may associate, forming larger aggregates, giving too high a value.

In like manner many pitfalls await the unwary in the interpretation of results got from osmotic measurements. It may often happen that the substance forms a loose compound with the solvent, which may pass unsuspected, and here again

dissociation and association of molecules will give abnormal results. Chloral hydrate in acetic acid is highly dissociated, giving a very large depression of the freezing-point, and in consequence a molecular weight in this solvent much above the normal. Phenol in benzene is another such case, and indeed it would seem to be a general rule that hydroxy compounds dissolved in benzene give abnormal values for the molecular weights determined by the lowering of the freezing-point, and, of course, similarly, by the raising of the boiling-point.

Furthermore, normal results can be obtained from freezing-point determinations only when the solvent freezes out in the pure state and forms no solid solution with the solute. In the case of the boiling-point method, it is essential that the vapour pressure of the solute should be negligible at the boiling-point of the solvent.

It has been our endeavour to present the determinations in a purely practical manner, aiming at results sufficient for all practical purposes, without the elaboration which would be necessary if the study were one of physical chemistry purely and simply. Nevertheless, it should always be the chief object of the experimenter to get the greatest possible accuracy of which the method and apparatus at hand will allow.

A. VAPOUR DENSITY DETERMINATIONS.

Victor Meyer's Method.

This well-known method is based on the measurement of the volume of air displaced by the vaporization of a known weight of a given substance. A sketch of the type of apparatus generally used for this purpose is given in Fig. 1.

The bulb of the outer jacket A is half-filled with a liquid

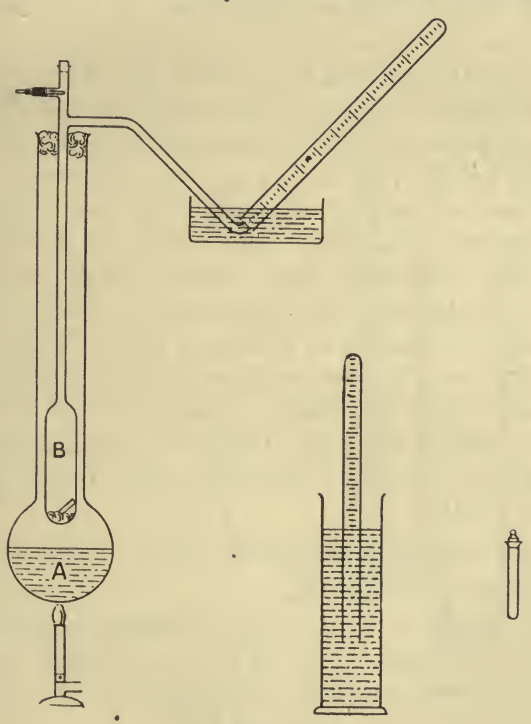

Fig. 1.

whose boiling-point is at least 30° higher than that of the substance whose vapour density is to be determined. A few pieces of porous porcelain are also put in to prevent bumping. By careful heating this liquid is boiled, and the bulb and stem of the inner portion B surrounded by vapour at a fairly steady temperature. The bulb of the inner portion B of the

apparatus contains a little cotton wool to break the fall of the bottle containing the given substance. The stem of B is provided with two side tubes, the one being the delivery tube leading to a water trough, and the other being connected to a glass rod of slightly smaller diameter by a piece of flexible rubber tubing. This rod stretches right across the stem and serves to hold the stoppered bottle containing the substance under examination until the conditions for the actual experiment have been obtained. Then by stretching the rubber tubing it can be dropped into the bulb of B without risk of air getting in or out of the apparatus.

The apparatus is dried by a current of warm air and the liquid in A heated to boiling. The substance under examination is weighed out into the loosely stoppered bottle provided, and placed on the rod, the cork being re-inserted. When bubbles cease to come into the measuring tube inverted over the delivery tube,[1] the rod is pulled back, and the bottle falls on the cotton wool in B. The stopper is blown out and the substance quickly vaporizes, displacing air, which is collected in the graduated tube freshly filled with water. When bubbles cease to come over, the measuring tube is carefully transferred to a cylinder containing water. The tube must be left for a little time before adjusting the levels, and the tension of aqueous vapour must be allowed for in the reduction of the volume to N.T.P.

Let x = weight of substance taken, whose molecular weight = M;

v = volume of air evolved reduced to N.T.P.

M gms. substance occupy 22,400 c.c. at N.T.P.

x gms. substance occupy v c.c. at N.T.P.

$$M = \frac{x \times 22400}{v}$$

Some common liquids used in the outer jacket are—

Water, B.P. 100°.	Ethyl benzoate, B.P. 260°.
Xylene, B.P. 140°.	β naphthol, B.P. 286°.
Aniline, B.P. 182°.	Diphenylamine, B.P. 310°.

[1] A gas burette provided at top with a 3-way tap is preferable for the collection of the displaced air.

Method of Bleier and Kohn.

This is a modification of V. Meyer's method, in which the pressure at constant volume produced by the vaporization of a known weight of substance is measured, instead of the volume at constant pressure. The adaptation of Meyer's apparatus for such measurements is shown in Fig. 2.

The delivery tube running to the gas measuring tube is cut off about 3 in. from the stem of the bulb and attached by pressure tubing to a T piece A. The vertical tube of this T piece is attached to another inverted T piece B of capillary tubing, provided with a 3-way tap, whilst the horizontal end of A connects directly with a manometer C, provided with a tap connexion G to the reservoir D, in the position shown in the sketch. The two limbs of C are provided with millimetre scales fixed in position.

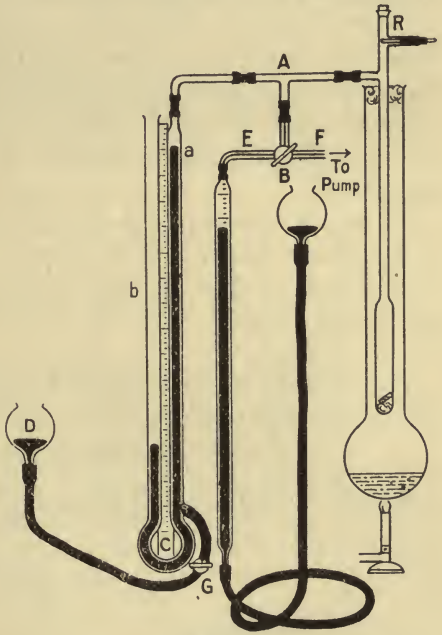

Fig. 2.

Before commencing a series of experiments it is necessary to determine the constant K of the apparatus, which may be defined as the increase in pressure produced by the introduction into the apparatus of 1 gm.-molecule of any gas at N.T.P. This constant can be determined in either of two ways :—

(*a*) By introducing a known volume of air under given temperature and pressure, and measuring the increase in pressure produced ; or,

(*b*) By measuring the increase in pressure produced by the vaporization of a known amount of a substance of given molecular weight.

(*a*) The tube E of the T piece B is connected to a gas burette containing dry air, at known temperature and pressure, over mercury. The other tube F of the T piece B is connected to a good water pump and the pressure inside the apparatus reduced to any desired extent. Then by careful manipulation of the reservoir D and the connecting tap G the mercury level in the right limb of C is brought up to a standard mark *a*. This is the constant volume mark of the apparatus, and the mercury level must always be accurately adjusted to this mark before taking pressure readings. Provided the mercury level remains constant at *a*, the reading on the left limb gives a measure of the pressure inside the apparatus.

B is now turned to put the apparatus and the gas burette in connexion and a certain volume of air drawn slowly into the apparatus. The mercury in C is again adjusted to *a* and the pressure read.

Let volume of air introduced, reduced to N.T.P. = V c.c., and let increase in pressure = x cms. mercury.

V c.c. produce an increase in pressure of x cms. mercury;

$\therefore$ 22400 c.c. produce an increase in pressure of $\frac{x \times 22400}{V}$ cms. mercury.

$$K = \frac{x \times 22400}{V}.$$

(*b*) The consideration of this method is given in the following paragraph.

Determination of the Molecular Weight of a Given Substance.—The liquid in the outer jacket of the bulb is gradually brought to the boil, and the known weight of substance contained in the usual small stoppered bottle gently dropped on to the rod R. The cork is inserted, and as soon as the liquid in the jacket is well boiling and the whole is at a

steady temperature, the apparatus is partially evacuated, the mercury in C adjusted to a, and the pressure read. When this keeps constant, the rod R is pulled back and the bottle allowed to fall on the glass wool at the bottom of the vaporizing tube. Vaporization is accompanied by increase in pressure. The fall of the mercury in C is roughly balanced by moving the reservoir D upwards so that at no time is the level in C far off the mark a. When vaporization is complete the level is again adjusted exactly to a and the pressure read.

Now 1 gm.-molecule of any substance gives increase in pressure of K cms. of mercury.

If x = weight of substance taken,

y = increase in pressure in cms. of mercury,

M = molecular weight of substance.

$$\text{Then } M = K\frac{x}{y}.$$

Dumas' Method.

This method is more of historic than practical interest. It requires a larger amount of material than other methods and takes longer to perform. The description here given will therefore be as brief as possible.

A clean dry glass bulb of 200-300 c.c. capacity, the neck portion being bent over and tapering to a capillary, is weighed and 2 to 3 c.c. of the liquid to be vaporized introduced into it. The flask is suspended in a bath of known constant temperature high enough to vaporize the liquid under examination. The air is thus expelled and a stream of vapour blown from the end of the capillary. When the flow of vapour ceases, the capillary is sealed off 2 to 3 in. from the open end, retaining the piece of glass thus drawn off

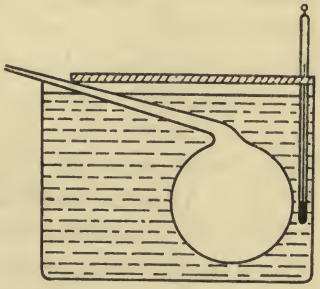

Fig. 3.

for weighing. The flask full of vapour is cooled and weighed. The closed end of the capillary is then opened under water which enters and fills the bulb. The whole is then again roughly weighed, so that the volume of the flask is known.

Wt. of flask + air = W gms.

Vol. of flask = V c.c.

$$\therefore \text{ Wt. of air in flask} = \frac{V \times \cdot001293 \times 273}{273 + t} \text{ gms.}$$

Where t = room temperature.

$$\text{Wt. of glass of bulb alone} = W - \frac{V \times \cdot001293 \times 273}{273 + t} \text{ gms.}$$

If wt. of flask and vapour = W_1 gms.

$$\text{Wt. of vapour} = W_1 - W + \frac{V \times \cdot001293 \times 273}{273 + t} = x \text{ gms. (say).}$$

If T = bath temperature,

$$\text{Wt. of V c.c. hydrogen at T} = \frac{V \times 273 \times \cdot00009}{273 + T} \text{ gms.}$$

$$= y \text{ gms. (say).}$$

$$\text{Vapour density} = \frac{x}{y}.$$

Hofmann's Method.

This method depends on the vaporization of the substance in a Torricellian vacuum at a constant temperature. Since the vaporization takes place under such low pressure the surrounding vapour need not be at a very high temperature so that steam is most often employed.

A graduated and calibrated closed tube, about 90 cms. long and 1½ cms. diameter, is filled with mercury (care being taken to get rid of all air bubbles), and inverted in a mercury trough. A thermometer is attached to it, and it is then surrounded by a jacketing tube fitted with corks and tubes for the entry and exit of steam. The level of the mercury is noted and also the air temperature. The small lightly stoppered Hofmann bottle containing a known weight of substance is introduced by pushing it under the mercury in the trough

and allowing it to rise up the tube into the vacuous space above the mercury.

Steam is then passed round this tube through the jacket; the substance vaporizes lowering the mercury level. When the latter is constant its level is again read and also the temperature. The level of the mercury surface in the trough

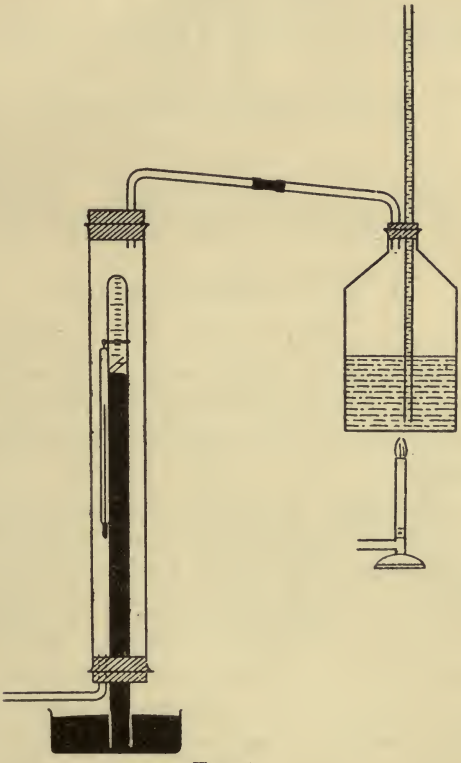

Fig. 4.

is taken and all the data necessary for a calculation of the vapour density of the substance are then to hand.

Let H = length of mercury column at t °C.

,, H^1 = ,, ,, ,, ,, ,, T °C.

Linear coefficient of expansion of mercury = 0·000181

$$\text{H reduced to } 0^\circ = \frac{H}{1 + 0{\cdot}000181t} = h.$$

$$H^1 \text{ reduced to } 0^\circ = \frac{H^1}{1 + 0{\cdot}000181T} = h^1$$

$(h - h^1) \times$ calibration factor = volume occupied by vapour at T° = V c.c.

$$\text{Volume of vapour reduced to N.T.P.} = \frac{V \times (h - h^1) \times 273}{760 \times (273 + T)} \text{ c.c.}$$

If W gms. = weight of substance taken.

$$\text{Vapour density} = \frac{W \times 760 \times (273 + T)}{V \times (h - h^1) \times 273 \times {\cdot}00009}$$

B. OSMOTIC DETERMINATIONS.

(*a*) Boiling-point Methods.

The molecular weight of non-volatile substances, that is to say, substances which do not vaporize appreciably at the boiling-points of the solvents employed, may be determined by the elevation which they produce in the boiling-points of these solvents.

One gm.-molecular weight of any such substance dissolved in a known weight or known volume of any such solvent produces a definite rise in temperature of the boiling-point, which rise is constant for every substance whose molecular weight in solution is normal, and is dependent solely on the nature of the solvent employed. Though theoretically only valid for infinite dilution, this method gives valuable results at moderate concentrations.

The required constant is the elevation which would be produced by the solution of 1 gm.-molecule of any substance in 100 gms. (*a*), or 100 c.c. (*b*), of the solvent—

Solvent.	*a*.	*b*.	B. Pt. (760 mms.).
Ethyl alcohol . . .	11·5	15·6	78·3 (Richter)
Acetone	16·7	22·2	56·5 ,,
Benzene	26·7	32·8	80·4 ,,
Chloroform	36·6	26·0	61·5 ,,
Water	5·2	5·4	100·0

Of these, chloroform is the best for general use as it is non-inflammable and has the maximum elevation. The method of calculation is quite simple, and can be best illustrated from an example.

0·572 gm. of the substance dissolved in 9·05 gm. of chloroform gave an elevation of 1·47°.

Let M = molecular weight of the substance.

An elevation of 36·6° is given by M gms. in 100 gms. $CHCl_3$.

An elevation of 36·6° is given by

$$\frac{9{\cdot}05}{100}\,\mathrm{M} \text{ gms. in } 9{\cdot}05 \text{ gms. } CHCl_3.$$

An elevation of 1·47° is given by

$$\frac{9{\cdot}05}{100}\,\mathrm{M} \times \frac{1{\cdot}47}{36{\cdot}6} \text{ gms. in } 9{\cdot}05 \text{ gms. } CHCl_3.$$

$$\therefore \frac{9{\cdot}05}{100}\,\mathrm{M} \times \frac{1{\cdot}47}{36{\cdot}6} = 0{\cdot}572.$$

$$\mathrm{M} = \frac{0{\cdot}572 \times 36{\cdot}6 \times 100}{9{\cdot}05 \times 1{\cdot}47} = 157.$$

The volume calculation is made in exactly the same way.

There are two well-known methods in general use for the determination of the elevation of the boiling-point. They differ principally in the method of bringing the solution to the boiling-point. In Beckmann's apparatus the indirect heat from a burner is used, whilst in the Landsberger-Walker method boiling is brought about by the introduction into the solution of the vapour of the solvent.

Beckmann's Method.

For ordinary laboratory practice the simplified apparatus shown in Fig. 5 is sufficiently accurate. The inner tube is dried and weighed with 2 to 3 in. of garnets. About 50 gms. of the solvent are put in and the whole re-weighed. The Beckmann thermometer is set for the boiling-point temperature, its bulb surrounded by a roll of platinum foil, and partially inserted among the garnets. This tube is surrounded by a wide glass tube which rests on the lowest of three asbestos boxes which have holes of different sizes cut in the upper and lower faces of each, the holes in the uppermost being the smallest. The inner tube rests on the top box and through the bottom of it is fused a thick short piece of platinum wire. The object of this, as well as the asbestos boxes and garnets, is to favour the formation of bubbles and so prevent superheating.

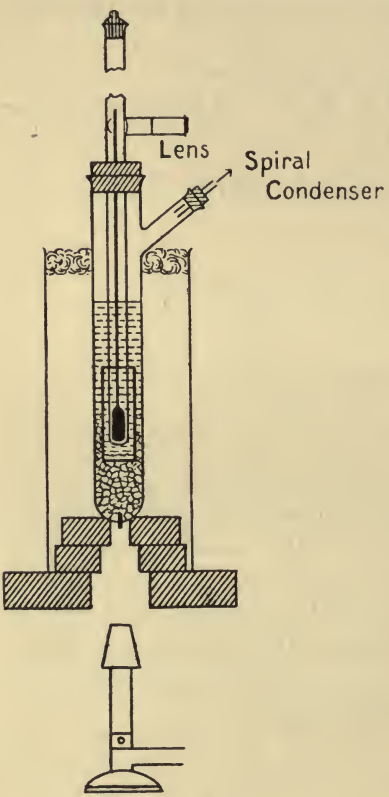

Fig. 5.

The space at the top between the outer glass vessel and the inner tube is filled up with glass wool to avoid cooling by the surrounding air. The side tube is connected to a spiral condenser and the condensed liquid falling back is prevented from coming into direct contact with the thermometer by the platinum foil which surrounds it.

The solvent is gently heated to the boiling-point and

when the temperature is fairly steady readings are taken for 15 to 20 mins. These should vary very little and their mean is taken as the boiling-point of the solvent.

About 1 gm. of the substance, if possible in the form of a pellet, is dropped through the side tube after removing the condenser, which is then replaced. The thermometer rises slowly to a maximum and gradually falls. This maximum temperature is taken as the boiling-point of the solution. A second determination is made immediately afterwards by adding another gram of substance and again noting the maximum rise.

The molecular weight is calculated as on p. 13. Two consecutive determinations for naphthalene in chloroform gave 126·3 and 129·5.

Landsberger-Walker Method.

The substance is dissolved in a pure solvent and the vapour of the solvent, produced by boiling in a separate vessel, is led into the solution which is itself surrounded by the vapour of the solvent. The elevation of the temperature at a particular moment, when the experiment is stopped, and the volume or weight of the solution, are noted. The apparatus usually employed for such determinations is shown in Fig. 6.

The small flask A (500 c.c.) is half-filled with the solvent, and a little porous porcelain is put in to prevent bumping. The flask is fitted with a safety tube and an exit tube, through which the vapour passes to the solution in B. This tube B, about $\frac{3}{4}$ in. wide, is graduated from the bottom in c.c. (usually up to 30 c.c.), and widens at the top to prevent the liquid's spurting through the hole E when the boiling is vigorous. The rubber stopper of B carries a delivery tube, at the bottom of which are four or five holes for the entry of the vapour of the solvent into the solution, and also a thermometer, which may be either a Beckmann or an ordinary thermometer graduated in $\frac{1}{10}$ths or a small range thermometer of greater sensitiveness. In all cases where possible,

it is best to set the thermometer so that the boiling-point temperature of the solvent comes just above the stopper, the

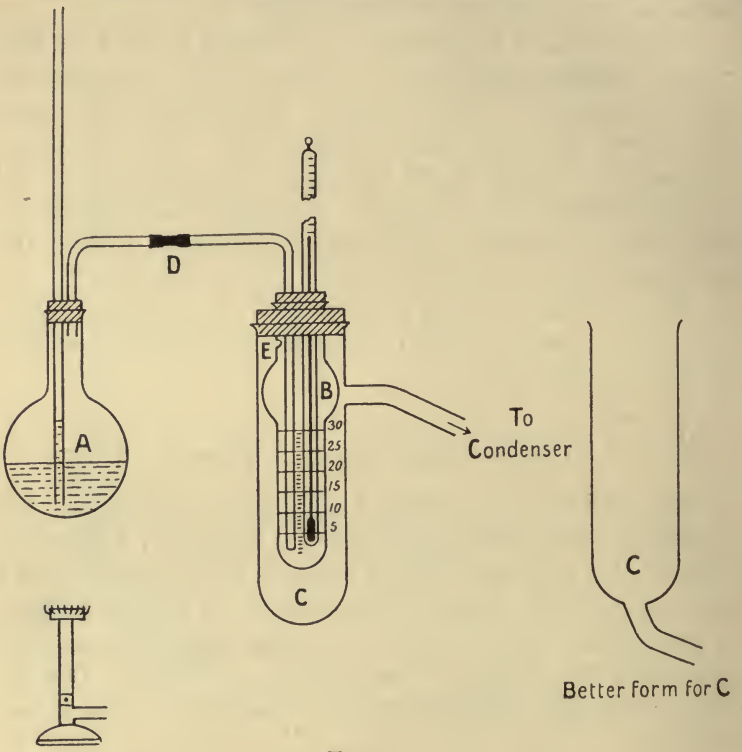

Fig. 6.

bulb of the thermometer being well in the liquid. B is surrounded by a tube C of larger dimensions into the stopper of which it fits fairly well. The tube C has an outlet connecting to an ordinary water condenser. In most forms of this apparatus the side tube is near the top of C and often on the same side as the hole E. In any case it must be on the opposite side, but better still is the modification shown in the sketch where the exit tube to the condenser comes from the bottom of C. This ensures that B is surrounded by vapour at constant temperature, viz. the boiling-point of the solvent (or a little lower). Ordinarily a large amount of solvent liquefies in C, greatly disturbing the temperature.

The apparatus having been fitted up, about 8 c.c. of solvent are placed in B, covering the bulb of the thermometer, and the vapour produced by boiling the solvent in A passed into it, at first quickly but afterwards more slowly till the rate of fall from the condenser to the receiver is about 1 drop per second. The temperature soon becomes quite steady and is then read off as the boiling-point of the solvent. Leaving about 8 c.c. of solvent in B, the remainder, as well as that in the receiver and that condensed in C, is put back into A. Preferably a pellet or lump, otherwise the powder, of about 0·5 gm. is dropped into B, allowed to dissolve and the vapour from A again led into it. When the rate of fall of drops into the receiver is again about 1 per second the temperature is again read and the entry of vapour at once stopped by breaking the connexion at D, guarding against risk of flame when dealing with an inflammable solvent. The stopper carrying the entry tube and thermometer is removed and the volume of the solution read off. A second determination may be made by using fresh solvent in B, or if there is room by adding another 0·5 gm. substance and noting the total rise for the total weight of substance in solution. At least five or six such determinations should be made with a maximum divergence of 5 per cent.

Greater accuracy is got by weighing the tube B empty and weighing again immediately after stopping the experiment. Deducting the weight of substance in solution from the total weight gives the weight of solvent present.

The necessary constants and mode of calculation have already been given on page 13.

Of the many other modifications of the original Landsberger apparatus only that recently devised by Dr. Paterson[1] will here be described.

The measuring vessel A (Fig. 7) is of the usual type but is enclosed in an outer jacket B furnished at the lower end with a hollow glass tap E having a hole of as large a diameter as

[1] "Proceedings of the Durham Philosophical Society," Vol. IV, Part 3, p. 142.

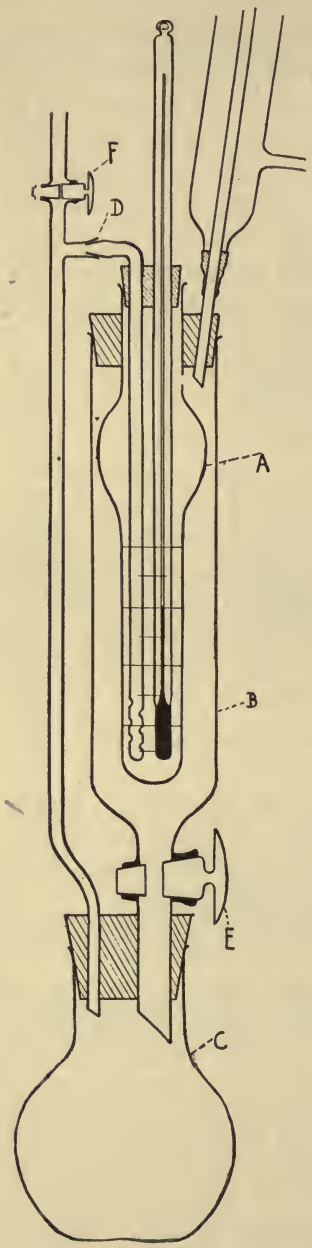

FIG. 7.—(From the "Proceedings of the University of Durham Philosophical Society".)

possible. The solvent is boiled in a small extraction flask C and the vapour may be passed into the measuring vessel by means of the side tube S. To allow of the removal of the stopper from the top of the measuring vessel this tube has a ground glass joint at D. The elbow at F is continued upwards and closed by means of a tap or a pinch-cock and a piece of rubber tubing. The tube S may be, with advantage, covered with cotton or asbestos to prevent undue condensation of the vapour.

The glass tap should be greased with some substance not readily soluble in the solvent used. Glycerine has been found useful in the case of benzene and allied substances and vaseline for the alcohols.

Method of Conducting the Experiment.—The boiling flask C is partly filled with the pure solvent and a few pieces of unglazed porcelain added to prevent bumping. The solvent is then boiled with the tap E open, until the whole of the inner tube A is raised to the temperature of the boiling solvent, i.e. until the solvent begins to drip back from the condenser. The tap is then closed, when the vapour will ascend the side tube and shortly the measuring vessel A will begin to fill with the liquid. When the thermometer registers a constant boiling-point, the Bunsen burner is re-

moved and the tap E simultaneously opened. The liquid which has collected above the tap flows back into the flask and causes a temporary cooling of the contents. This is sufficient to cause the solvent which has boiled into A to be sucked back into the flask.

A weighed quantity of the substance whose molecular weight is to be determined is then introduced into A and the tap carefully closed to such an extent that some of the vapour continues to pass up through it and warm the outer jacket, while the rest passes up the side tube D. When a sufficient quantity of the liquid has collected in the measuring vessel and a definite temperature is noted the tap E is again opened, but, to prevent the liquid from sucking back into the flask, the tap F is opened at the same time. The volume of the liquid and the temperature are then noted and the tap again partly closed.

The experiment is repeated at various dilutions until the measuring tube is filled, the readings being taken as before.

Good results are readily obtained, even by beginners, with this compact piece of apparatus since the control over the concentrations of the solutions is better than with other forms.

(*b*) Freezing-point Method.

The principle is exactly analogous to that of the boiling-point methods just described. One gm.-molecular weight of any substance dissolved in a definite amount of solvent lowers the freezing-point of that solvent by a definite amount dependent only on the nature of the solvent, provided that the substance has a normal molecular weight in the solvent selected. It is necessary for this method that the solvent should freeze out independently of the solute and not form solid solutions with it, and furthermore absolute accuracy is confined to infinite dilution, but moderate concentrations give results of sufficient accuracy for ordinary work.

The constants (a) for the solvents usually employed are given below. The method of weighing being the only one applicable to this case, the figures represent the lowering of

the freezing-point produced by the solution of 1 gm.-molecule of the solute in 100 gms. of solvent.

Solvent.	a.	F. Pt.
Acetic acid (anhydrous) . . .	39·0	17·0°
Benzene	50·0	5·5°
Water	18·6	0·0°

Beckmann's Apparatus.

The apparatus in general use for this method is due to Beckmann and is shown in Fig. 8.

It consists of an outside vessel A containing the freezing mixture, whose nature depends on the solvent, but should be so arranged that its temperature is not more than 3° to 4° below the freezing-point of the solvent. It is provided with a stout iron stirrer, and in the middle of it is placed the air-jacketing tube B. Through the cork of B passes the inner tube C (provided with a side tube near the top), which contains a known weight of the solvent. This can be got, either by calculation from the density of a known volume put in, or by directly weighing the tube C before and after the introduction of the solvent. C is provided with a stirrer of platinum and a Beckmann thermometer, which is set for the experiment, the bulb, of course, being well in the liquid.

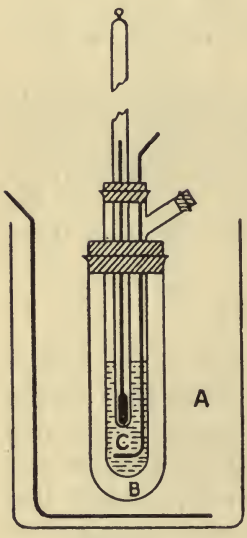

Fig. 8.

When the apparatus has been fitted together ready for the experiment, the solvent is stirred continuously and uniformly. The freezing mixture in A is likewise given an occasional stir up to ensure uniformity of temperature. The readings of the Beckmann gradually fall, and when the temperature indicated is a little below the actual freezing-point of the solvent as determined roughly by a preliminary experiment,

the liquid is stirred a little more vigorously when the temperature usually rises and the solvent begins to freeze out. The maximum temperature reached is read off by a lens as the freezing-point of the solvent. The tube C and contents are then removed and the solid mass melted by holding in the hand. It is then replaced and a second determination of the freezing-point made. The mean of three consecutive readings, which should show good concordance, is taken as the freezing-point of the solvent.

C is now again removed, the solid melted as previously, and a weighed amount (0·5 gm.) of the powdered substance dropped in through the side tube. The powder dissolves more readily in the cooled solution than does a lump or pellet. When solution is complete, a determination of the new value of the freezing-point is got from a second set of three consecutive concordant readings.

Another 0·5 gm. of the powder is dissolved in the solution and the total lowering again found.

The calculation is exactly the same as for the boiling-point methods. The error should be within 5 per cent.

CHAPTER II.

ULTIMATE ANALYSIS.

I. Estimation of Carbon and Hydrogen.

Method of Liebig.

The following apparatus and materials are required :—

1. A hard glass tube cut to fit the furnace.
2. A U-tube containing pumice stone moistened with strong H_2SO_4.
3. A Geissler tube containing potash solution.
4. Two bubblers containing strong H_2SO_4.
5. Two large glass storage vessels containing air and oxygen, respectively, over water.
6. Apparatus for drying the above gases.
7. Porcelain boat.
8. Oxidized and reduced copper spirals.
9. Coarse copper oxide (oxidized copper wire).
10. Coarse lead chromate contained in a copper spiral.

The tube is cut to fit the furnace and is cleaned with concentrated H_2SO_4 and $K_2Cr_2O_7$, rinsed with water and dried. It is filled with dry ignited coarse copper oxide, to the length shown in the diagram, being kept in place by short, tightly fitting copper spirals (Fig. 9).

The lead chromate spiral and the oxidized copper spiral are placed in the tube and the latter is then burnt out by passing dry air through it whilst it is heated to redness. The air is passed through the purifier, whilst a bubbler is placed at the other end of the combustion tube. When the tube is red-hot, oxygen is passed instead of air and this current is maintained for about 20 minutes. The oxygen is then replaced by air and the tube is allowed to cool down.

At this stage the boat, which has been ignited, cooled in a desiccator and weighed, containing a known weight of the substance under investigation is introduced at the place shown, the oxidized copper spiral being introduced at the end, immediately preceding the porcelain boat. The freshly reduced copper spiral is now placed at the end of the combustion tube remote from the boat.

The series of dry, weighed absorption tubes is then attached to the tube, a calcium chloride guard tube being joined to the sulphuric acid bubbler.

The burners under the copper oxide are now lighted to within 4 in. of the boat and also under the reduced spiral. Air is sent through the apparatus at the rate of two bubbles a second, the rate being indicated in the H_2SO_4 bubbler.

The covering tiles of the furnace are now gradually dropped in position over the hot oxide. When this part of the tube is at a dull red heat, burners are

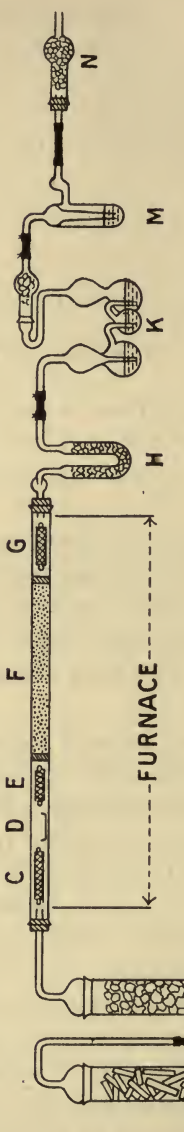

FIG. 9.

AA'. Towers containing stick potash. BB'. Towers containing fused calcium chloride. C. Oxidized copper spiral. D. Porcelain boat. E. Spiral containing fused lead chromate, or silver gauze. F. Coarse copper oxide. G. Reduced copper spiral (when nitrogen is present). H. Tared U-tube containing pumice moistened with sulphuric acid. K. Potash bulbs weighed with calcium chloride tube. M. Sulphuric acid bubbler. N. Calcium chloride guard tube.

lighted under the oxidized copper spiral and tiles are placed over this end of the combustion tube. Burners are now gradually turned on in a direction towards the boat, the ideal condition being to distil the substance slowly on to the cold portion of the copper oxide and lead chromate and to complete the combustion slowly.

When the volatile portion has distilled in this way, dry oxygen is substituted for the air and heating is extended along the whole tube. Oxygen is passed until the boat is perfectly clean, i.e. until all carbon residue has been burnt away.

At this stage air is again passed instead of oxygen, to replace the latter gas in the absorption vessels, for about 15 minutes. Any moisture condensed in the ends of the tube is driven over by heating with a small flame or by a hot tile.

At the end of this period, the absorption tubes are removed, disjointed, and the ends of each absorption vessel are protected by caps. They are allowed to stand for some time in near proximity to the balance and are then re-weighed (without caps).

Increase in weight of the U-tube containing pumice stone and H_2SO_4 = weight of water produced.

Increase in weight of the Geissler and bubbler tubes = weight of CO_2 produced in the combustion.

Example. — Sulphanilic acid $C_6H_4\begin{matrix}SO_3H\\NH_2\end{matrix}$

Weight of boat and substance		4·4502 gms.
Weight of boat . . .		4·3308 gms.
Weight of substance . .		0·1194 gm.
Geissler tube	(*a*)	50·7066 gms.
	(*b*)	50·8890 gms.
Increase		0·1824 gm.
H_2SO_4 bubbler	(*a*)	22·0839 gms.
	(*b*)	22·0840 gms.
Difference		0·0001 gm.
Pumice stone tube	(*a*)	37·7252 gms.
	(*b*)	37·7696 gms.
Increase		0·0444 gm.

$$\text{Percentage carbon} = \frac{3}{11} \times \frac{0{\cdot}1824 + 0{\cdot}0001}{0{\cdot}1194} \times \frac{100}{1} = 41{\cdot}66$$

$$\text{Percentage hydrogen} = \frac{1}{9} \times \frac{0{\cdot}0444}{0{\cdot}1194} \times \frac{100}{1} = 4{\cdot}13$$

By calculation C = 41·59 per cent.
H = 4·1 per cent.

The following points with regard to the method of procedure in combustions of this type should be noted by a beginner :—

(1) Do not heat up or cool down the combustion tube too rapidly or the glass will soon fracture.

(2) Do not attempt to carry out the combustion too rapidly or low results will be obtained by incomplete combustion.

(3) Do not heat too strongly that portion of the tube (*a*) containing lead chromate which may fuse ; (*b*) containing silver in cases where halogens are present as the silver salts are volatile.

(4) Be very careful that all rubber connexions are quite firm. Pressure tubing is preferable and should be wired on—the ends of the glass tubes should also touch.

(5) A 30 per cent solution of potash should be used for absorption of the carbon dioxide. More concentrated solutions than this tend to deposit carbonates during the combustion which clog up the apparatus. In no case should the potash in the bulbs be used for more than two determinations.

(6) Do not lower the gas burners or turn off the air current before disconnecting the absorption vessels, or back-suction of the potash will occur.

(7) The tube of H should just reach inside the stopper of the combustion tube, otherwise water tends to collect at this point and is difficult to dissipate without softening the stopper.

Estimation of Carbon and Hydrogen in an Organic Liquid.

Method due to J. Walker.

The principle of this method is the same as in that of Liebig. The tube is, however, of narrower bore and is shorter. Oxygen is passed through the tube, heated in the furnace, to burn out carbonaceous matter from the coarse copper oxide, and the tube is cooled, with oxygen still passing at the rate of one bubble per second.

When cool, some of the copper oxide is removed into a dry tube, and a glass capsule containing the weighed liquid is introduced. The whole is then replaced in the combustion tube and heating is proceeded with in a manner identical with that adopted in the method of Liebig.

The water is collected in a weighed calcium chloride tube, and the CO_2 absorbed in two U-tubes containing soda lime. The speed of the oxygen current is shown by a sulphuric acid bubbler.

The U-tubes in the burning-out process are filled with oxygen, and the taps on each tube are closed. They are then weighed full of oxygen instead of air. After the combustion, which is quicker in this method, the tubes are again weighed full of oxygen. The percentages of carbon and hydrogen are calculated, as before, from the weights of CO_2 and H_2O respectively, produced in the combustion.

Notes.—If the liquid is practically non-volatile at ordinary temperatures it may be weighed out in the boat as with solids. It is safer, however, to weigh the liquid in any case in a small tube closed at one end and provided with a loosely-fitting stopper. The tube is introduced into the combustion tube in a slightly-inclined position by means of the porcelain boat. The loosely stoppered end of the tube is arranged towards the copper oxide filling.

With exceedingly volatile liquids it is necessary to use small glass bulbs which have been weighed. These are easily made (see hydrolysis of esters and Fig. 26) and are filled by

placing them in a vacuum desiccator with the capillary tube immersed in the organic liquid.

On allowing the pressure inside the desiccator to become atmospheric, liquid rises into the bulb. The capillary is dried and sealed and the whole weighed.

Before introduction into the combustion tube, the end of the capillary is broken off and all placed in the porcelain boat.

Heating in the case of volatile liquids must be very gradual as there is every likelihood of an explosion taking place if the liquid is distilled too rapidly.

Estimation of Carbon and Hydrogen in Presence of Halogens.

The copper halide which is formed may be volatile to a certain extent or decomposed by oxygen, yielding free halogen. The passage of the latter into the absorption tubes is prevented by placing a coil of silver in the combustion tube near the exit and keeping it at a moderate temperature in the furnace.

In the standard method described for the determination of carbon and hydrogen, the place of silver gauze is taken by lead chromate which has been fused and broken into lumps. Lead halides are less volatile and more stable than copper halides. It is advisable that the chromate should not be heated too strongly if a halogen is present.

In the case of some aromatic bodies rich in bromine, it is found that the lead bromide retains some carbon giving low results for the latter. It is thus advisable to use the silver coil in such combustions.

The lead chromate also serves to retain the sulphurous and sulphuric acids produced by the combustion of sulphur compounds. Lead sulphate is more stable than cupric sulphate at high temperatures.

After the combustion of the sulphur compound it is advisable to test the condensed water in the bulbs of the drying tubes for sulphuric or sulphurous acids.

Compounds Containing Alkali or Alkali Earths.—When these metals are present, the compound is mixed with lead chromate or potassium bichromate before combustion. If these means are not adopted, CO_2 is retained in the form of metallic carbonate.

II. Estimation of Carbon and Hydrogen Using a Catalyst.

Method of Dennstedt.

"Anleitung ver. Elementaranalyse," III, 1910.

The principle underlying this method consists in passing a mixture of the vaporized substance and oxygen over a catalyst such as platinum, platinized quartz or platinized asbestos. By using such a method no special furnace is needed and consequently less burners are required.

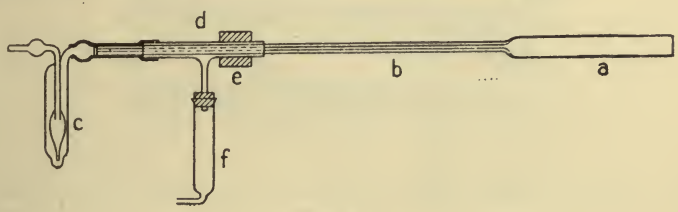

Fig. 10.

The apparatus consists of a combustion tube 80-90 cms. in length placed on an iron bed covered with asbestos paper to prevent cracking.

A layer of catalyst (4-5 cms. long) is placed near the middle of the furnace tube.

The author recommends conducting the combustion with a double supply of oxygen, which can be effected by using a tube as shown in Fig. 10. It consists of an inner tube (*a*) 18 cms. long, which when introduced into the combustion tube allows a clear space of 2-4 mm. between the two tubes. It is made of hard glass and is left open at one end; its purpose is to hold the porcelain boat and organic material.

The other end is fused to a 25 cms. capillary tube (*b*),

which is connected to a wash bottle (*c*) containing a few c.c. of concentrated sulphuric acid.

A T-piece of glass tubing (*d*) is placed over the capillary tube in such a manner that one end is secured by the rubber tubing which joins the wash bottle (*c*) to the capillary tube (*b*).

The stopper (*e*) fits into the combustion tube. The T-piece is connected to a drying tube containing calcium chloride, which, in its turn, is attached to the drying apparatus. A current of hot oxygen may be passed by this means into the combustion tube between the inner and outer tubes.

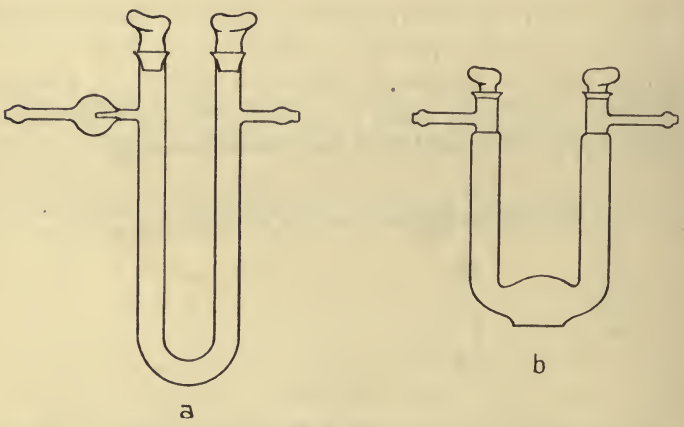

Fig. 11.

Absorption Vessels.—Dennstedt recommends a calcium chloride U-tube of the form depicted, for the water. The side tubes should be closed by glass rod and rubber tubing during weighing operations (Fig. 11 *a*).

It is recommended also to fill the tube so that the limb next to the combustion apparatus is half-filled with cotton wool. This allows of the easy removal of the hydrated calcium chloride.

Cotton-wool plugs are also fitted on the top of the calcium chloride in each limb to prevent the loss of calcium chloride dust into the side tubes.

The carbon dioxide is absorbed by means of soda lime[1] contained in a U-tube provided with ground-in stoppers (Fig. 11 *b*). A U-tube is connected to this, having calcium chloride in one limb and soda lime in the other; by this means the last traces of carbon dioxide are removed and the water lost from the soda lime is retained in the carbon dioxide estimation tubes.

Following this tube is a small wash bottle containing a 1 per cent solution of palladous chloride which indicates the rate of passage of unabsorbed gases, but serves more particularly to indicate any carbon monoxide which produces a turbidity, in which case the combustion is useless and must be repeated.

Preparation of Palladium Chloride Solution.—Shake 1 gm. of pure $PdCl_2$ with 100 c.c. water till no more seems to dissolve. Filter off and use. The remaining solid

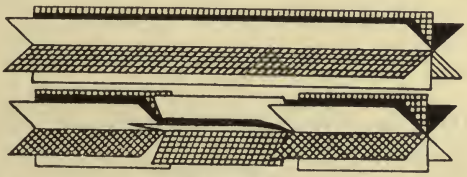

Fig. 12.

is treated with quantities of 100 c.c. water successively in the above manner.

Preparation of the Contact Surface.—The best surface is thin platinum foil about 10 cms. long and 0·1 mm. thick, bent into a six-edged star-shaped section, loosely fitting into the combustion tube. The efficiency of the foil is proportional to its thinness, the latter being, of course, limited to that degree allowing of its being easily handled.

The section may be cut into three lengths, the middle one turned round a little from the others so as not to leave a free passage for the gases. This combination presents three sets of sharp edges and is naturally more efficient (Fig. 12).

When poisoned by traces of volatile metals such as lead,

[1] Perfectly dry soda lime must be previously moistened with one c.c. of water, as it does not easily absorb carbon dioxide.

zinc, tin, arsenic, etc., the catalytic power of the platinum can be revived by boiling in concentrated hydrochloric acid, or, in the case of lead, by aqua regia.

Platinized quartz is prepared by warming suitable fragments free from iron in an alcoholic solution of pyridine platini-chloride. The treated quartz is then dried and ignited in a blow-pipe flame. It must be replatinized frequently and must be tested before a combustion by heating it in a Bunsen flame, turning out the flame, and ascertaining whether the gas is re-ignited by the hot surface.

Dennstedt prefers platinum foil to this reagent.

The Combustion.—The substance is weighed out into a boat which is then introduced into the apparatus. The latter

Fig. 13.

must be tested in order to ascertain whether the joints are perfectly airtight.

The contact material is heated and a stream of oxygen is passed through the tube. By the system of double streams of oxygen employed, the analysis is finished, with complete combustion, in shorter time than usual in such determinations.

The bed of the furnace under the platinum foil must be red-hot, the end of the foil near the boat being also in a glowing condition. The substance is volatilized by a burner placed half-way between the end of the tube and the boat. The combustion may be said to be proceeding correctly so long as the platinum foil is in an incandescent state. In the absence of nitrogen, sulphur, and halogens, the remainder of the combustion tube is heated to 200° to remove all water vapour (Fig. 13).

Nitrogen Present.—Oxides of nitrogen are absorbed by means of lead peroxide placed in a large porcelain boat (14

cms. long)[1] which is introduced into the end part of the combustion tube. Since water acts on lead nitrate giving a basic nitrate and liberating nitric acid which is not all absorbed by the lead peroxide, it is necessary to mix Pb_3O_4 with the PbO_2. This is easily done by heating the lead dioxide in the tube previous to the combustion. The red lead produced is then mixed with fresh dioxide and the boat filled with the mixture. The boat should fill the tube and preferably should be open towards the contact substance. It is heated to a temperature of 300°-320° and must be replaced in a second determination.

Preparation and Purification of the Lead Dioxide.—A half-saturated solution of lead nitrate acidified with nitric acid is electrolyzed with a platinum foil anode and a platinum foil or wire cathode. Lead dioxide is formed on the cathode in heavy crystals. The latter are boiled with dilute nitric acid to remove free lead, and then with water. After drying, it is powdered and passed through a sieve (144 meshes to sq. cm.), being then placed in a round bottom flask and treated successively with nitric acid and with water.

It is dried in a current of washed, dry air whilst gently heated and is finally roasted at a temperature of 350°. In the preparation, all contact with organic substances, filtration, drying in hot ovens, or drying in ordinary air must be rigorously avoided. Air always contains sulphur dioxide, and this renders the lead dioxide useless for determinations of sulphur.

At 350° almost all the tenaciously held water of hydration is driven off and a small portion is split off by transformation to red lead. This has no deleterious action as the temperature of a combustion does not rise high enough to cause this latter action.

Estimation of Sulphur, Carbon, and Hydrogen.—In this determination three boats (8 cms. long) are filled with the mixed oxides of lead, the first boat being placed 5-7 cms. from the platinum star, the others touching one another.

[1] If much nitrogen is present two boats are used, the second being 8 cms. long, the first being 5 cms. from the platinum star.

After the combustion the boats are drawn out carefully with a copper wire provided with a small hook. The lead oxide is knocked out into a small beaker, the boats being then placed in sufficiently long, dry, clean test tubes.

The boats are washed in the test tubes with a 5 per cent solution of sodium hydrate (free from sulphate), warmed by placing in boiling water, and the alkali poured off into the beaker.

An appreciable amount (up to 25 per cent) of sulphur remains in the combustion tube as SO_3 so that the combustion tube, entry tube, and platinum must be washed with water and the washings (20-30 c.c.) added to the beaker.

The boats are treated twice more with alkali until the total amount of liquid is about 90 c.c. The mixture is warmed on the water bath for one hour, stirring up the residue to prevent bumping.

It is filtered, made up to 101 c.c. (sp. gr. $PbO_2 = 7$, and about 7 gms. are used) with washings, 25 c.c. taken, acidified with hydrochloric acid, warmed and precipitated with a hot solution of barium chloride. The sulphur is calculated to 100 c.c. of solution. Should the amount of sulphur only be required, then pure calcined sodium carbonate is used to absorb the sulphuric anhydride.

Four gms. of such sodium carbonate are placed on three small boats placed quite close to the platinum star. In place of absorption vessels, a short glass tube leads into a small washing tube for observing the rate of flow of the gas. The combustion is carried out in the usual manner but at a temperature of 400°.

The sodium carbonate is dissolved in water, and the washings from the combustion tube, entry tube, and platinum added to the solution. After oxidation of sulphite with a few drops of bromine water and boiling, it is acidified with hydrochloric acid, the excess of bromine boiled off, and precipitated as barium sulphate.

Estimation of Halogens.—Halogens are converted by combustion over catalytic platinum partly to halogen acids and the remainder to free element. They are estimated by

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means of silver foil or gauze or by molecular silver.[1] The silver is heated to 500°-600° to prevent the formation of silver nitrite or nitrate.

Twenty gms. of silver powder are placed in a porcelain boat (14 cms. long) which is situated near the contact substance, and heated to 500°-600°.

The PbO_2 boat is present as usual and is heated to 350° to prevent the formation of lead halides.

The boat and silver contents are reweighed, the increase giving weight of halogen.

The silver halide is dissolved out with a solution of potassium cyanide followed by washing well with hot water.

It is better to place a boat of lead dioxide (8 cms.) in front of the molecular silver to absorb any oxides of nitrogen produced.

Determination of Halogen and Sulphur Together.—The following method is applicable in the presence of nitrogen :—

The SO_3 combines with the silver forming silver sulphate and the SO_2 is absorbed by the lead oxides.

The lead oxides are treated, after the combustion, with aqueous alkali as explained above, filtered, and washed. The washings from the tubes and platinum are added to the filtrate and the whole acidified with hydrochloric acid.

The powdered silver is extracted several times with boiling water to dissolve the silver sulphate which is filtered from the residue of silver and silver halide.

The filtrate is acidified with hydrochloric acid, well boiled, filtered again from the precipitated silver chloride, and the filtrate and washings added to the extraction liquor from the lead oxides.

In the combined liquid the sulphate is estimated in the usual manner.

The residue of silver (and halide) is treated with dilute potassium cyanide solution, filtered, and washed well. The filtrate is acidified with dilute nitric acid, the silver halide precipitated and estimated as usual.

[1] Prepared by treating silver halide residues with granular zinc.

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Combustion of Volatile Liquids.—In the case of easily volatile liquids, such as benzol, it is convenient to volatilize them outside the combustion tube in apparatus shown in Fig. 14.

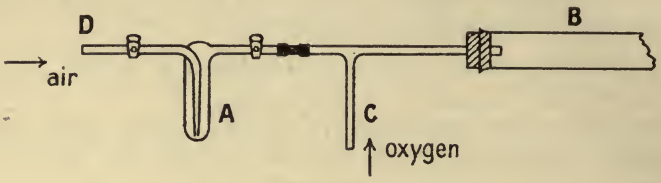


Fig. 14.

A. A small bubbler provided with suitable side tubes and stop cocks. A small quantity of the liquid is drawn into this and the taps closed. All traces of liquid are removed from the side tubes beyond the tap.

B. The combustion tube provided with a platinum star and lead peroxide as in Dennstedt's method.

C. A T-piece, by means of which a current of pure oxygen is admitted to the combustion tube.

D. A delivery tube connected to a purified, dry air supply.

Procedure.—Oxygen is passed at a slow rate by means of the T-piece, then the taps of A are opened and a steady current of air allowed to bubble through the liquid. The final traces of liquid are removed by immersing A in a hot water bath at the requisite temperature. We have found that this method gives concordant results in the case of commercial benzol. The sulphur alone may be estimated as in Dennstedt's method, adopting sodium carbonate instead of lead peroxide.

Note.—Using lead peroxide, it was found necessary to treat the platinum foil with aqua regia after each experiment, as the catalytic powers were reduced considerably owing to poisoning.

Modification of Dennstedt's Method.

Walker and Blackadder ["Chem. News," 1909, **99**, 4].

A furnace 60 cms. long is recommended, and copper oxide is used instead of platinum stars or platinized materials.

Thirty gms. of dehydrated oxide are taken for the determination, part being placed in the tube and the remainder being mixed with the substance in a stoppered tube. This mixture is transferred to the combustion tube, the stoppered tube being washed out several times with dry cupric oxide.

The method of procedure is identical with that given by Dennstedt. Time of experiment is about half an hour.

Marck ["Jour. prakt. Chem.," 1906, **73**, 359].

In this method an oxidized copper coil (5 cms. long) is introduced into the tube, being surrounded by asbestos so that it fits securely into the combustion tube.

The substance is weighed out in a porcelain boat, and this is introduced into a hard glass tube closed at one end. The open end of this tube is about 4 to 10 cms. from the coil of copper oxide.

Julius Bekk ["Ber.," 1913, **46**, 2574].

The author used asbestos fibre, coated with cerium dioxide, as a catalyst in the combustion of organic compounds in ordinary or Dennstedt combustion tubes.

The catalyst was prepared by impregnating asbestos with cerium nitrate and igniting strongly.

The substance is placed in a narrow tube, drawn out at one end to a jet, near the oxygen inlet. A length (30 cms.) of the catalytic agent is placed after the substance and is heated to a dull red heat.

In the case of substances containing sulphur or nitrogen, a short layer of PbO_2 is recommended. The combustion takes 15-20 minutes to complete; halogens may be estimated by a silver spiral or by molecular silver.

The catalyst, unlike platinum, is not poisoned by As_2O_3 or PbO_2.

III. Estimation of Carbon and Hydrogen Using an Electrical Method.

In such methods platinum is used as a catalyst, using an inner tube for the purpose of carrying the boat and substance as in the Dennstedt method. The source of heat is a coil of platinum-iridium placed inside the combustion tube, the coil being brought to a red heat by means of a suitable electric current.

See Breteau and Lerona ["Bull. Soc. Chem.," 1908 (4), 3, 15]; Blount ["Analyst," 1905, **30**, 29]; Tucker ["J. Amer. C. S.," 1907, **29**, 1442], and Morse and Gray ["Amer. Chem. J.," 1906, **35**, 451].

Estimation of Oxygen in Organic Compounds.

M. C. Boswell ["J. Amer. Chem. Soc.," 1913, **35**, 284].

The quartz tube for combustion is about 98 cms. long by 13 mm. internal diameter, and is loosely filled with pieces of charcoal for a length of 40 cms. from a point 13·5 cms. from one end. The tube is heated in an ordinary furnace from which the iron trough and tiles have been removed, two guards of asbestos board being arranged to prevent preliminary heating of the organic material, one 15 mm. from the end of the charcoal, and the second 3 cms. from the first.

The stream of hydrogen used in the combustion is prepared electrolytically, the oxygen being removed by passing the gas through a quartz tube (36 cms. × 1·3 cms.) containing a coil of copper gauze heated very strongly. The hydrogen is dried successively in $CaCl_2$, H_2SO_4 and P_2O_5 tubes.

The absorption vessels are arranged as follows:—

(1) A U-tube containing pumice and H_2SO_4.

(2) Soda lime tube.

(3) U-tube with pumice and H_2SO_4 to guard (2).

(4) Modification of Levy's iodine pentoxide apparatus heated to 160°-170° in oil bath.

(5) U-tube with pumice and H_2SO_4 to guard (4).

(6) Soda lime tube.

(7) U-tube with pumice and H_2SO_4.

(8) Guard tube of $CaCl_2$.

Method.—About 0·3 gm. substance is weighed into a silica boat previously ignited and weighed, which is then placed in the tube at a distance not less than 6 cms. from the nearer asbestos guard.

The tube is swept out with hydrogen and then the absorption tubes are connected.

Heating is now commenced and extended gradually towards the silica boat. The current of gas is continued for at least 15 minutes from the time when the substance has been fully heated, the rate being increased during the last 10 minutes. The combustion should take from $1\frac{1}{2}$ to $1\frac{3}{4}$ hours. At the end of this operation, the five tared absorption vessels are detached and dry air (free from CO_2) is passed through them for about 10 minutes, when they are separated and allowed to cool for an hour with the ends guarded with rubber tubes and pieces of glass rod.

The whole of the oxygen is converted into water, CO_2 and CO. The H_2O is absorbed in the first H_2SO_4 pumice tube, the CO_2 in the soda lime tube (2) weighed with (3), while the CO is estimated by passing the gas over iodine pentoxide in (4), absorbing the CO_2 produced in (6) and (7).

In calculating the increased weight in the tubes (6) and (7) a deduction of 50 per cent is made for the oxygen produced from the iodine pentoxide.

Note.—In the case of substances yielding compounds of carbon and hydrogen which may condense in the absorption vessels, it is advisable to mix a weighed quantity of an agent such as potassium permanganate with the original substance.

Additional references.—M. C. Boswell ["J. Amer. Chem. Soc.," 1914, **36**, 127] for compounds of lower oxygen content. Also "Ann.," **90**, 288; **117**, 247; "Zeit. anal. Chem.," **6**, 136; **7**, 272; **13**, 1; **15**, 371; "Comp. rend.," **55**, 432.

Estimation of Nitrogen. (Dumas.)

Historical Survey.—In the original method of Dumas, a closed combustion tube was used, the carbon dioxide necessary for sweeping out the nitrogen being evolved by the heating of sodium hydrogen carbonate placed at the sealed end of the tube. The combustion of the organic matter was brought about by heated copper oxide.

In a later modification of the method, Maxwell Simpson ["J. C. S.," 1853, **6**, 290] used magnesite for the production of carbon dioxide, and a mixture of copper and mercuric oxides as the oxidizing agent.

Groves ["J. C. S.," 1880, **37**, 300] produced carbon dioxide in a tube connected to the combustion tube. In this way the latter was preserved for several determinations.

The present method, using an open tube, is due to Warrington ["J. C. S.," 1882, **41**, 346].

The nitrogen measuring vessels usually employed are of the type suggested by H. Schiff ["Zeit. anal. Chem.," **7**, 430] and by Groves (loc. cit.).

Apparatus and Materials required :—

1. Combustion tube 3 in. longer than the furnace bed.
2. Coarse and fine copper oxide.
3. Copper spirals.
   10 cms., 6 cms., and two short ones (2 cms.).
4. CO_2 apparatus.
5. Nitrometer, with 50 per cent KOH solution.
6. Mortar, and copper funnel.

The copper oxide is heated in porcelain basins in a muffle furnace and allowed to cool, finally in a desiccator.

The 10 cm. spiral is reduced by heating and plunging into a vapour of methyl alcohol. It is dried at 100° and cooled in a desiccator.

The oxidized spiral (2 cms.) is then placed into position at A and a long layer of coarse copper oxide introduced. Following this is placed a short length of medium-sized copper oxide (Fig. 15).

A known weight of substance is placed in the mortar with

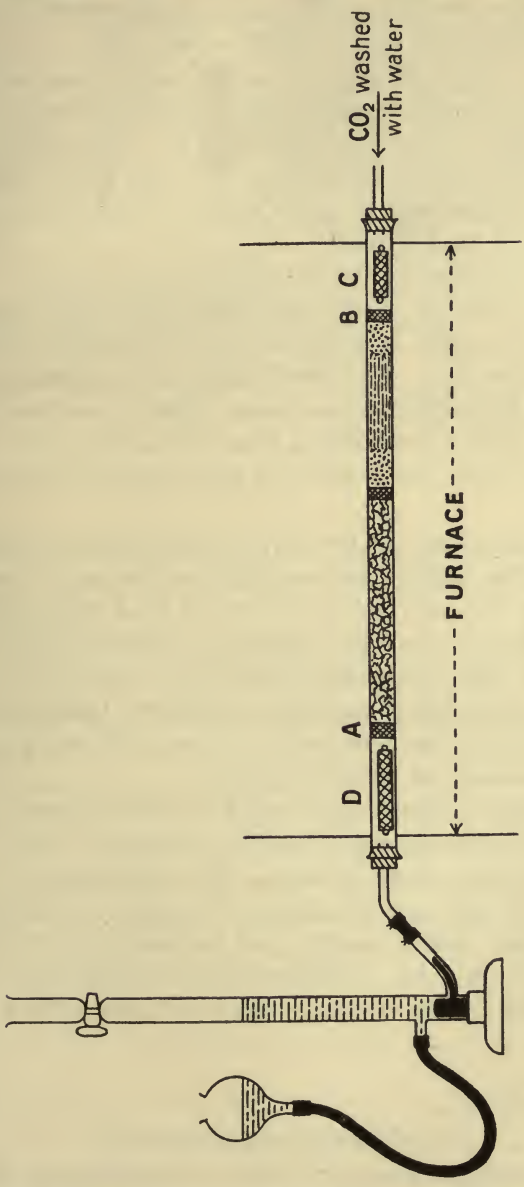


FIG. 15.

fine copper oxide, and an intimate mixture is made. This is

introduced into the tube through the funnel. The mortar is washed out several times with small quantities of fine copper oxide and the washings are added to the tube.

A short length of medium copper oxide is now added and then a short length of coarse oxide; finally the short oxidized spiral (2 cms.) is placed in position at B. The oxidized spiral (6 cms.) is now placed in position at C, the tube is tapped to secure a free passage of gases along its length and is then placed on the cold furnace.

The dry reduced spiral is now introduced at D. Asbestos boards are fitted as shown in the diagram, and the end near the reduced spiral is attached to a nitrometer containing 50 per cent potash. The other end of the combustion tube is connected to a CO_2 generator from which a very slow current of CO_2 is passed through the tube. Meanwhile, the burners are lighted from the nitrometer end to within 4-6 in. of the substance.

When all the air has been expelled from the tube (indicated when all the bubbles are entirely absorbed in the potash of the nitrometer), the nitrometer tube is filled with potash, the tap is turned off, and the supply of CO_2 is cut down. The heating is now commenced under the oxidized spiral and gradually extended towards the substance, taking care that the evolution of gas does not exceed two bubbles in the tube of the nitrometer at the same instant.

When the combustion is ended, the CO_2 stream is turned on again and the residual nitrogen is swept out. This operation takes about 10-15 minutes. The nitrometer is now removed and the gas is allowed to come to atmospheric temperature. After reading the barometer, the volume is corrected to N.T.P. The tension of KOH solution may be taken as $\frac{1}{3}$ that of water vapour at the same temperature.

Example :—

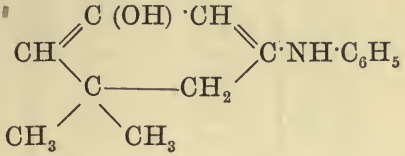
Weight substance, 0·1210 gm.

Barometric pressure, 760·2 mm. Temperature, 22° C. Volume gas, 16·8 c.c. Tension water vapour at 22° = 19·7 mm.

Percentage Nitrogen

$$= \frac{16{\cdot}8 \times (760{\cdot}2 - 6{\cdot}6) \times 273 \times 100 \times 0{\cdot}001259}{760 \times 295 \times 0{\cdot}1210} = 15{\cdot}68.$$

Notes on Estimation of Nitrogen by Dumas' method:— P. Haas ["J. C. S.," 1906, **89**, 570] has shown that certain basic hydroaromatic substances containing two methyl groups attached to the same carbon atom yield appreciable quantities of methane when treated with cupric oxide. This of course is measured with the nitrogen. By using lead chromate instead of cupric oxide or by mixing the compound with cupric oxide and cuprous chloride this does not occur.



T. Gray ["J. Soc. Chem. Ind.," 1898, **17**, 743] has shown that nitric oxide is not obtained if the following conditions are observed:—

The copper coil in the front of the combustion tube should be 5 in. in length and should just fit the tube when tightly rolled up. This coil must be strongly heated during the experiment, and the current of CO_2 must be stopped during the actual combustion operations.

Dunstan and Carr found that normal results were obtained only when the hydrochloride of conidine was burnt, otherwise the nitrogen is contaminated with varying amounts of methane. If methane be passed over CuO 40 per cent escapes. All is oxidized to CO_2 and H_2O if Cu_2Cl_2 be present.

Pressure of aqueous vapour in millimetres of mercury (Regnault).

Temp. C.	Pressure.	Temp. C.	Pressure.	Temp. C.	Pressure.
0·0	4·6	10·5	9·5	20·5	17·9
0·5	4·8	11·0	9·8	21·0	18·5
1·0	4·9	11·5	10·1	21·5	19·1
1·5	5·1	12·0	10·5	22·0	19·7
2·0	5·3	12·5	10·8	22·5	20·3
2·5	5·5	13·0	11·2	23·0	20·9
3·0	5·7	13·5	11·5	23·5	21·5
3·5	5·9	14·0	11·9	24·0	22·2
4·0	6·1	14·5	12·3	24·5	22·9
4·5	6·3	15·0	12·7	25·0	23·5
5·0	6·5	15·5	13·1	25·5	24·3
5·5	6·8	16·0	13·5	26·0	25·0
6·0	7·0	16·5	14·0	26·5	25·7
6·5	7·2	17·0	14·4	27·0	26·5
7·0	7·5	17·5	14·9	27·5	27·3
7·5	7·8	18·0	15·4	28·0	28·1
8·0	8·0	18·5	15·8	28·5	28·9
8·5	8·3	19·0	16·3	29·0	29·8
9·0	8·6	19·5	16·9	29·5	30·7
9·5	8·9	20·0	17·4	30·0	31·7
10·0	9·2				

Estimation of Nitrogen.

Method of Kjeldahl.

Take a known weight of the organic substance, and wash it into a round bottom flask with a fairly long neck, using about 20 c.c. concentrated sulphuric acid. Heat the flask over a very small Bunsen flame nearly to boiling point for about an hour. Now add about 8 gms. of powdered K_2SO_4 and heat again for about $\frac{3}{4}$ hour.

The nitrogen of the organic substance is now in the form of ammonium sulphate.

The contents of the flask are now transferred to the flask of an ammonia distillation apparatus taking care to wash out the first flask thoroughly. Dilute with 100 c.c. water.

The ammonia distillation is carried out in apparatus shown in the diagram (Fig. 16).

A. Contains the sulphuric acid and ammonium sulphate.

B. Contains strong NaOH solution, and is plugged by means of a glass rod provided with an india-rubber cap made from a short length of rubber tubing.

C. Contains standard acid in excess of that required to neutralize the ammonia produced.

D. A tube containing glass beads moistened with water. This dissolves any traces of NH_3 which might escape from the acid.

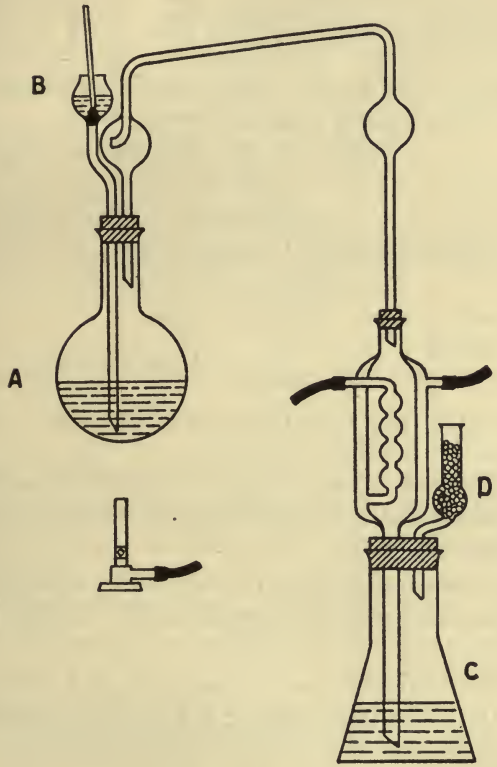


Fig. 16.

When the apparatus is fitted up as shown, a few drops of methyl orange are added to A, and excess of NaOH is allowed to run in cautiously from B.

The flask A is now heated by a Bunsen flame, and the contents are boiled for about 20 minutes. Caustic alkali is added from time to time from B.

At the end of this time, the stoppers of A and C are re-

moved, the condenser is washed out with distilled water into C, and the contents of C are titrated with standard alkali, using methyl orange as indicator.

Example.—Weight of substance, 0·4422 gms. (acetanilide). Volume of acid used for absorption, 50 c.c. N . H_2SO_4. This volume is made up to 1000 c.c.

Alkali 25 c.c. $\equiv$ 16·35 c.c. $\frac{N}{10}$ H_2SO_4.

Titration—mean result. 25 c.c. alkali $\equiv$ 35·0 c.c. solution.

Hence 1000 c.c. acid solution contain—

$$\frac{1000 \times 16{\cdot}35 \times 0{\cdot}0049}{35} \text{ gms. } H_2SO_4$$

$$= 2{\cdot}289 \text{ gms.}$$

Hence, acid neutralized by ammonia =

$$2{\cdot}45 - 2{\cdot}289 = 0{\cdot}161 \text{ gm.}$$

Hence percentage of nitrogen equals—

$$\frac{0{\cdot}161 \times 28}{98} \times \frac{100}{0{\cdot}4422} = 10{\cdot}40 \text{ per cent.}$$

Percentage N in acetanilide = 10·37 per cent.

Notes on the Kjeldahl method :—

1. Nitrites and nitrates may be removed by heating with ferrous sulphate and hydrochloric acid. Warrington [" Chem. News," 1885, **52**, 162].

2. Nitro-compounds may be reduced by heating with 0·5 gm. of sugar or 2 gms. of benzoic acid. Asboth [" Chem. Zent. (3), **17**, 161].

3. Pyridine, quinoline, azo-compounds, and nitrites may be treated in the following manner : 0·5 gm. substance is heated with 0·5 gm. of anhydrous copper sulphate, 1 gm. of mercury, 2 gms. of phosphoric oxide, 1 gm. of sugar, and 20 c.c. of concentrated sulphuric acid. In the case of nitrates, 2 gms. of benzoic acid are added also. C. Arnold [" Arch. Pharm." (3), **24**, 785].

4. Benzene, pyridine, and quinoline derivatives can be decomposed by dissolving 0·2 to 0·8 gm. in 20 c.c. concentrated sulphuric acid, to which is added (cool) crystalline potassium bichromate 0·5 gm. at a time to an extent 0·5 gm. in excess of the quantity required to oxidize the substance. The flask

is then heated on a water bath to remove gaseous decomposition products until the liquid is pure green in colour. M. Krüger [" Ber.," 27, 609].

5. The important modification of the original method whereby potassium sulphate is introduced in the decomposition flask is due to Gunning [" Zeit. anal. Chem.," 28, 188]. Mercury was added by Dyer [" J. C. S.," 1895, 67, 811].

6. Bodies difficult of decomposition by the Kjeldahl method are sodium nitroprusside, phenylhydrazine, compounds rich in chlorine, and nitrates. In this connexion see " J. Amer. Chem. Soc.," 17, 567 ; " Analyst," 1905, 314 ; " Proc. C. Soc.," 1901, 25, 351, and 1903, 27, 988 ; " Ber.," 1905, 38, 559.

7. Other information on the method may be obtained by consulting " Zeit. anal. Chem.," 23, 551 ; 24, 439 ; 25, 424 ; 26, 249 ; " Chem. News," 1888, 57, 62.

Estimation of Nitrogen by Soda Lime.

Will and Varrentrapp [" Ann.," 1841, 39, 257].

Certain nitrogenous bodies when heated with soda lime yield ammonia, but this method is not general in its application, e.g. in the case of nitro- and azo-compounds, ammonia is not obtained.

A combustion tube, 30 cms. long and 6 mm. in diameter, is drawn out to a point and slightly bent at this end (Fig. 17).

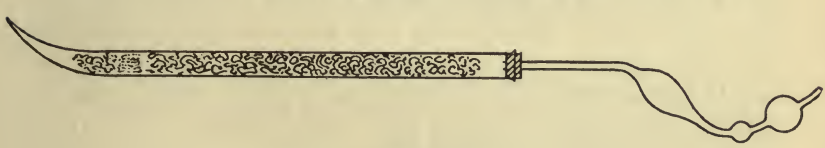


Fig. 17.

A small quantity of ignited granular soda lime is placed in the closed end, and this is followed by a thorough mixture of the substance with ignited powdered soda lime (1 : 10), the mortar being rinsed out with soda lime several times. The rest of the tube is filled with soda lime and the open end is connected by a rubber stopper to bulbs containing standard acid.

The tube is placed in a furnace, tapped to produce a free air space and heated from the bulbs towards the closed end until the whole is hot.

The free end of the bulb is attached to a water pump, so that the tube is evacuated partially. The closed end of the combustion tube is then broken off, so that a current of air is drawn through the apparatus; this sweeps out all the ammonia into the absorption bulbs. The bubbles should not be faster than two per second, and the acid should not become discoloured or cloudy.

Estimation of Halogens.

The principle underlying the method of Carius is that, by the destruction of the organic matter by means of nitric acid in a sealed tube at 200° C. the halogen may be made to react with pure silver nitrate also present in the tube. The silver halide is removed and the halogen estimated in the usual manner.

The tube is prepared in the following manner: A stout walled soda glass tube of 20 mm. outside diameter and about 40 cms. length is carefully sealed at one end. Care must be taken that the thickness of the glass in the bulb is equal to that of the tube itself. This is effected by allowing the glass at the sealed end to become fairly thick by manipulation in a blow-pipe flame. By blowing into the tube fairly gently, at the same time imparting a rotatory motion to the tube, the sealed end acquires an even thickness of wall. The end must now be thoroughly annealed in a luminous flame and then set aside in a place free from draughts.

The tube is now thoroughly cleansed with a mixture of strong sulphuric acid and potassium dichromate, rinsed several times with distilled water and then put in an inverted position to drain. It is finally dried by heating in an oven and by blowing in a current of air.

A quantity of the substance under investigation is introduced into a clean, dry, weighed specimen tube, and the

whole is weighed. While the next operations are in progress, this tube is transferred to a desiccator.

The dry bomb tube is fixed in an upright position and about 0·5 gm. $AgNO_3$ free from halogen is dropped in. By means of a delivery tube reaching to the bottom of the Carius tube, about 5 c.c. fuming HNO_3 are added to the bomb tube. Care must be taken that in withdrawing the delivery tube no drops of liquid are allowed to come into contact with the walls of the bomb tube.

The tube and contained organic body are now allowed to slide into the bomb tube so that the nitric acid does not come into contact with the contents of the small tube.

The open end of the bomb tube is now carefully heated up until it softens. A piece of glass rod is now fused on to the end of the tube; by suitable pressure a thorough union is produced between the two.

The tube may now be sealed off at a point near to the end. Care must be taken that, in the whole procedure, the tube is kept in an inclined position so that the contents of the specimen tube are not brought into contact with the nitric acid.

The glass tube is first heated up and allowed to thicken considerably, yet equally all round. When this has been accomplished, the tube is withdrawn from the flame and drawn out to a capillary tube which is then sealed off in a very small flame. The end is now thoroughly annealed as described above.

When cold the tube may be placed in a horizontal position. It is then wrapped in a layer of stout paper and placed in an iron tube of a furnace. The paper ensures equal heating and freedom from scratching.

The heating must be gradual; the time taken to reach the final temperature should be about two hours. The oven is then kept at 200° from two to three hours, and then allowed to cool whilst still holding the bomb. Owing to the high pressure now within the tube, it must be carefully handled and wrapped in a cloth so that only the capillary tube protrudes from the packing. Any liquid is first removed by

gentle heating, and then the capillary tube is softened in the blow-pipe flame, which allows the pressure to blow out the contained vapours.

The end of the tube is now cut off by means of a glass cutter and hot iron ring.

The contents of the tube are now carefully turned out into a beaker and the tube rinsed out thoroughly with water. The end of the tube which has been cut off is also thoroughly washed, and the washings added to the beaker.

The specimen tube is removed and washed with water.

The contents of the beaker are now heated with continual stirring and then filtered through a paper, the ash of which is known. The residue is washed with dilute nitric acid until all soluble silver salts have been removed. The silver halide, when dry, is detached from the filter paper and placed in a dry, weighed crucible. The filter paper is then rolled in a coil of platinum wire and ignited in the usual manner, the ash being added to the contents of the crucible. The ash, when cold, is moistened with HNO_3 and then with a drop of the acid corresponding to the halogen under consideration.

The crucible is now gently heated until the edges of the silver halide show signs of fusion. After cooling in a desiccator, the crucible and silver halide are weighed. The weight of silver halide is thus found and the percentage of halogen in the organic compound can then be easily determined.

Example :—

Weight of tube and tribromaniline	2·1220	gms.
Tube	1·9657	,,
Tribromaniline . . .	0·1563	,,
Weight of crucible, ash, Ag Br .	24·4621	gms.
Crucible	24·1961	,,
Ash and Ag Br . . .	0·2660	,,
Ash	0·0001	,,
Ag Br	0·2659	,,

$$\text{Percentage bromine} = \frac{80 \times 0{\cdot}2659 \times 100}{188 \times 0{\cdot}1563}$$

$$= 72{\cdot}38.$$

Percentage bromine in $C_6H_2Br_3{\cdot}NH_2 = 72{\cdot}72$.

Estimation of Sulphur.

Carius Method.

In estimating sulphur, the silver nitrate is omitted, and only 2 c.c. HNO_3 are used. The liquid and washings from the tube are acidified with HCl and boiled. Hot barium chloride solution is then added, the mixture boiled, and the precipitated $BaSO_4$ allowed to settle. The $BaSO_4$ is filtered off, dried, and weighed. The percentage of S can then be calculated.

Example :—

Weight of tube and substance .	3·4910	gms.
Tube	3·1834	,,
Substance	0·3076	,,
Weight of crucible and $BaSO_4$.	17·6813	,,
Crucible	17·2728	,,
$BaSO_4$	0·4085	,,

$$\text{Percentage S} = \frac{32{\cdot}07 \times 0{\cdot}4085 \times 100}{233{\cdot}44 \times 0{\cdot}3076}$$

$$= 18{\cdot}25.$$

Method of Piria and Schiff.

This method can be employed only, as in the case of fusion with potash, when the substance is non-volatile. It should be used with substances which are incompletely decomposed with fuming nitric acid and silver nitrate.

About 0·1 to 0·3 gm. of the substance is mixed with an intimate mixture of lime and dry sodium carbonate (4 : 1) in a small platinum crucible, the latter being completely filled with the alkaline mixture and then inverted in a larger one, the space between the two being filled with the same mixture.

The crucibles are heated over a blow-pipe flame so that the external portions acquire a high temperature before the organic substance commences to break down. After heating completely to redness, the crucibles and contents are cooled, being finally extracted with water.

The aqueous liquid is rendered acid with dilute nitric acid at a low temperature, filtered, excess of silver nitrate added, warmed, and the silver halide collected and weighed in the usual manner.

Should iodine be present, sodium carbonate alone is employed as calcium iodate is soluble in water. The aqueous extract is acidified, and iodine destroyed with a minimum amount of a solution of sulphur dioxide.

The iodide is estimated in the usual manner as silver halide.

In the case of liquids, only those forming loose compounds with alkalis should be analysed by the above method, as loss by volatilization may occur.

Method of Stepanow ["Ber.," 1906, **39**, 4056].

0·2 to 0·3 gm. of the substance is introduced into the flask of a reflux apparatus with 20-40 c.c. of 98 per cent alcohol. The flask is heated on a water bath. Excess of metallic sodium is dropped down the condenser so as to produce a continuous, vigorous reaction.

$$XCl + 2Na + C_2H_5OH = XH + NaCl + C_2H_5ONa.$$

The amount of sodium used should be 25 times the requisite quantity required by the above equation.

The mixture is diluted with 20-40 c.c. water and the alcohol distilled off.

The sodium halide is determined by Volhard's method after making the aqueous residue strongly acid with dilute nitric acid.

The author obtained good results with halogenated benzene nuclei and cinnamic acids.

Two halogens in the substance may be easily determined by this method.

The precipitated silver halides are removed and weighed. The excess of silver nitrate is also found by titration and the relative amounts of the halogens found by calculation.

Bacon ["J. Amer. Chem. Soc.," 1909, 41, 49] gives the following as essential details for Stepanow's method. He states that the amount of sodium required for the various halogens is as follows :—

If the weight of substance is a (about 0·2 gm.), then $156a$ is the number of c.c. of 98 per cent alcohol required if chlorine be present, $68a$ c.c. if bromine, and $44a$ c.c. if iodine be present.

Add to the solution in a reflux apparatus, $19{\cdot}5a$ gms., $8{\cdot}5a$ gms., $5{\cdot}5a$ gms. of sodium for chlorine, bromine, and iodine respectively.

The time taken for the addition of sodium should be *at least* half an hour, and the mixture should then be boiled for an hour.

Cool to 50°-60°, dilute with water down the condenser, and estimate the halogen by Volhard's method.

Method of L. H. Berry ["Chem. News," 1906, 94, 188].

About 0·2 gm. of the compound is weighed in a small platinum crucible, which is then filled with a mixture of anhydrous sodium carbonate and calcium oxide (1 : 5).

When iodine has to be estimated, sodium carbonate only should be used.

The crucible is then inverted in a larger platinum crucible and the space between the two is filled up with the same mixture.

The larger crucible is then heated with a blow-pipe, commencing at the bottom, until the whole is red-hot. After half an hour's heating the mass is cooled and is then decomposed with a sufficiency of cold dilute nitric acid (1 : 4). The halogen is now estimated by Volhard's method.

Estimation of halogens in presence of sulphur by sodium peroxide :—

Pringsheim ["Ber.," 1908, 41, 4267].

A given weight of the substance is mixed in an iron crucible with sodium peroxide, using an iron nail as a stirring rod.

Amounts of peroxide required :—

Substances with more than 75 per cent of C + H + S, eighteen times, and those with 50-75 per cent C + H + S, sixteen times the weight of substance.

Compounds with 25-50 per cent of C + H + S are mixed with half their own weight of a compound rich in C and H, and the mixture added to sixteen times its weight of peroxide.

Substances with less than 25 per cent of C + H + S are mixed with their own weight of a compound such as sugar, and eighteen times their weight of peroxide.

The crucible is placed in a vessel of cold water. The reaction is commenced by heating the nail to a red heat and introducing it into the crucible through a hole in the lid.

Sulphur.—The mass is extracted with water, acidified with HCl and the S estimated with $BaCl_2$.

Halogens.—Reduce the extracted aqueous solution with 3 c.c. of a saturated solution of $NaHSO_3$ to reduce chlorates, etc., and add dilute sulphuric acid to dissolve the iron precipitate.

Boil off SO_2 and estimate the halogen in the usual manner, with nitric acid and silver nitrate.

Estimation of Iodine.

The Carius method yields erratic and unreliable results with iodine compounds.

Linneman ("Ann. Chem. Pharm.," 1871, **160**, 205) states that the discrepancies are due to the solubility of silver iodide in nitric acid containing an excess of silver nitrate.

A. F. Seeker and W. E. Mathewson (Circular 65, U.S. Department of Agriculture) have observed crystals of free iodine in the bomb, although ample excess of silver nitrate has been present. They state that some free iodine is lost in transferring the mixture from the bomb tubes.

Other methods suggested for the estimation of iodine in the presence of other halogens relate chiefly to soluble inorganic compounds. In applying these to organic substances a preliminary destruction of the organic matter is necessary. Care must be taken in fusion with alkaline carbonates, as reducing sulphur compounds may be produced from sulphonated dyes. These must be removed before the application of Reinige's method ["Zeit. anal. Chem.," 1870, **9**, 39]. The distillation requires much attention to prevent the loss of iodine during the driving off of the chlorine in the method of Baubigny and Rivals ("Comp. rend.," 1903, **137**, 927).

In the methods mentioned above, the iodide is oxidized by permanganate to iodate.

Seeker and Mathewson suggest the following procedure in the analysis of substances, such as erythrosin ["Chem. News," 1911, **103**, 61].

Place 0·3 to 0·4 gm. of the sample in a porcelain dish, dissolve in 5 c.c. of a 10 per cent solution of sodium hydrate, add 35 c.c. of a 7 per cent solution of permanganate, cover with a watch glass and add 10 c.c. of nitric acid. Heat cautiously with frequent agitation on a steam bath until all action ceases. Remove the cover glass and evaporate to dryness, during which operation no reducing gases must have access to the mixture. Treat the residue with 5 c.c. of a 7 per cent permanganate solution and 5 c.c. of concentrated nitric acid and again take to dryness. Now take up with about

50 c.c. water and 5 c.c. of nitric acid following with 40 c.c. of a saturated solution of sulphur dioxide. Break up the pieces with a glass rod, and stir until the hydrated manganese oxide has dissolved.

Add an excess of silver nitrate to the clear solution and boil to drive off excess of sulphur dioxide. Filter off the aggregates of silver iodide and weigh in the usual manner.

This procedure may be adopted with volatile and easily saponified compounds, e.g. iodoform, but it need only be employed in cases where other halogens are present in admixture.

Estimation of Sulphur.

Method of Carius (previously described), p. 53.

Sodium Peroxide Method (Edinger).

Mix 0·2 to 0·8 gm. with concentrated sodium peroxide solution in a platinum vessel and evaporate on a steam bath and finally over a small flame. Care is taken that spirting and explosions do not occur. If blackening occurs, more peroxide should be added.

The vessel and its contents are finally transferred to a basin containing a solution of sodium peroxide. The whole is heated for a quarter of an hour on the water bath, the vessel removed and washed, the liquid acidified with hydrochloric acid, and the sulphur estimated as barium sulphate in the usual way.

Method of Hermann Apitzsch ["Zeit. angew. Chem.," 1913, 26, 503].

In this method the substance is burnt in a current of oxygen with the use of a catalytic agent. The combustion tube is drawn out, the narrow end being joined to an apparatus containing a solution of sodium hypobromite. The substance is weighed in a porcelain boat, which is then placed in position in the combustion tube. Special spirals of platinum gauze are placed on both sides of the boat, the combustion

being brought about by careful heating in a current of oxygen. At the end of the combustion, the tube is washed out with water, the washings being added to the contents of the absorption tube. The sulphur is now estimated as sulphate in the usual manner, giving results claimed to be accurate. The author states that this method is preferable to that of Carius.

In the case of volatile substances, the liquids are vaporized in a tube outside the combustion apparatus.

Method of Isidore Bay ["Comp. rend.," 1908, **146**, 333].

The compound is heated in a tube with sodium carbonate and calcined magnesia, a current of oxygen being passed through the tube during combustion. The contents of the tube are dissolved in dilute hydrochloric acid, and the dissolved sulphates precipitated with barium chloride in the usual way.

The tube is filled as follows :—

A plug of asbestos fibre 3 cms. in length is placed at the end; then 10 cms. of a mixture of sodium carbonate and magnesia (1 : 1); next, the compound to be investigated mixed with sodium carbonate and magnesia, and, finally, another layer of the mixture about 20 cms. in length. A plug of asbestos fibre is employed to close this end of the tube.

The exit of the tube is connected to a Liebig bulb containing sodium hydrate and bromine to prevent loss of sulphur compounds.

A blank test is performed with the carbonate and magnesia mixture.

In the case of liquids, the substance is introduced into the combustion tube in a small glass tube.

	Carius.	Bay.
C_2H_5SH	51·6 per cent sulphur.	51·55 per cent sulphur.
$(C_2H_5)_2S$	35·53 ,, ,, ,,	35·55 ,, ,, ,,
$(C_3H_5)_2S$	28·07 ,, ,, ,,	28·00 ,, ,, ,,
$C_4H_3S.COOH$	25·16 ,, ,, ,,	25·75 ,, ,, ,,
C_4H_4S	38·09 ,, ,, ,,	38·02 ,, ,, ,,

Estimation of Sulphur in Coal.

Method of Eschka.

0·5 to 1 gm. finely pulverized sample is mixed with one and a half times its weight of a mixture of ignited magnesia and anhydrous sodium carbonate (2 : 1) in a platinum crucible, with a glass rod. The mixture is covered with a thin layer of the basic materials, and the crucible is inserted in a hole in a sheet of asbestos cardboard, which is placed over a small Bunsen, in an inclined position. By this means the lower portion only of the crucible is brought to a dull red heat.

The contents of the crucible are frequently stirred with a thick platinum wire so as to hasten the oxidation of sulphur to sulphate. The grey colour of the mixture should vanish completely and change to a yellow, brown, or red colour within an hour.

The mass is extracted with hot water, and bromine water added until the liquid assumes a yellowish tint. The clear liquid is decanted off and the residue washed with hot water.

The liquid is acidified with hydrochloric acid and the bromine boiled off. A slight excess of a boiling solution of barium chloride (or barium nitrate) is added to the boiling solution and the precipitated $BaSO_4$ is weighed in the usual manner.

A blank experiment is performed with the magnesia and sodium carbonate.

1 part $BaSO_4 \equiv 0{\cdot}1373$ parts sulphur.

Estimation of Carbon Disulphide and Total Sulphur in Commercial Benzene.

[Edward S. Johnson, "J. Amer. Chem. Soc.," 1906, **28**, 1209.]

Carbon Disulphide.—The carbon disulphide is converted into potassium xanthate by addition of saturated alcoholic potash ; this is removed from the benzene by repeated washings with alkaline water. The xanthate is then converted into the copper compound by adding acetic acid in very slight excess and precipitating with copper sulphate. The precipitate is collected, washed, and ignited to oxide.

In practice 1 part of oxide = 1·75 parts CS_2.

Total Sulphur.—Five c.c. of the sample are introduced into a small vaporizer, through which is passed a slow current of hydrogen; this and the benzene vapour are then burnt in a special apparatus in oxygen and the products of combustion are absorbed in bottles containing sodium carbonate and bromine solution; this causes a complete conversion of the sulphur into sulphuric acid which may be estimated gravimetrically.

Or, the products of combustion may be collected in a standard solution of sodium hydrate, to which neutral hydrogen peroxide is added, and the excess of alkali titrated with standard acid.

Sulphur in Fuels.

[I. C. Allen and I. W. Robertson, "8th Int. Cong. App. Chem.," 1912, 10, 25, and "Tech. Paper," 26, U.S. Bureau of Mines.]

Review of Methods:—

1. Dry fusion with alkalis and subsequent oxidation with bromine.
2. Dry fusion with alkalis and oxidizing agents.
3. Wet treatment with alkalis and oxidizing agents.
4. Carius method and modifications of it.
5. Burning in lamp.
6. Burning in oxygen at atmospheric pressure.
7. Burning in current of oxygen.
8. Burning in calorimetric bomb.

Notes.—Method (6) due originally to Hempel and modified by Gräfe ("Zeit. angew. Chem.," 1904, 17, 616) is inaccurate.

Methods (1), (2), (3) are trustworthy for solid fuel but not for oils.

Methods (4) and (7) are accurate, but require great attention as they are somewhat dangerous.

Method (5) is, of course, restricted to oils which can be so burnt.

[Vide Conradson, "8th Int. Cong. App. Chem.," 1912, 1, 133.]

Estimation of Phosphorus in Organic Compounds.

1. Oxidation by nitric acid as is effected in Carius method for determining the halogens and sulphur is suitable for the estimation of phosphorus. The substance is heated in a bomb tube with fuming nitric acid as has already been described, silver nitrate being, of course, omitted in this case. The phosphorus is thereby converted into phosphoric acid.

The solution is rendered alkaline by adding ammonium hydrate and the phosphate precipitated with "magnesia mixture" and estimated as $Mg_2P_2O_7$.

Magnesia mixture.—Mix together 1 part of crystallized magnesium sulphate, or chloride, 2 parts of ammonium chloride, 8 parts of water and 4 parts of ammonium hydrate (0·88), allow to stand for some days, and decant the clean liquid.

After the addition of slight excess of magnesia mixture the liquid is stirred vigorously without touching the walls of the vessel with the glass rod, and allowed to stand for some hours.

The precipitate is washed with dilute ammonia until all soluble ammonium salts are removed. It is dried in an oven and ignited at red heat in a platinum crucible until of constant weight. The percentage of phosphorus may be easily calculated from the weight of $Mg_2P_2O_7$ obtained.

Wt. of $Mg_2P_2O_7 \times 0{\cdot}27838$ = weight of phosphorus.

2. R. H. A. Plimmer and W. M. Bayliss ["J. Physiol.," 1905, 33, 439].

In a course of experiments on the separation of phosphorus from caseinogen by enzymes and alkali, the authors adopted the following procedure which is essentially that of A. Neumann ["Zeit. physiol. Chem.," 1902, 37, 129].

The organic matter is oxidized with a mixture of equal parts of nitric and sulphuric acids, and the phosphoric acid precipitated as ammonium phospho-molybdate. The latter is washed free from acid and dissolved in excess of $\frac{N}{2}$ alkali, the excess being titrated with $\frac{N}{2}$ acid.

The difference × 1·268 = milligrams P_2O_5.

Neumann states that not more than 40 c.c. of the oxidizing mixture should be employed on account of the difficulty encountered in the precipitation of phospho-molybdate due to excess of sulphuric acid. The authors found it necessary to modify this condition ; 10 c.c. of concentrated sulphuric acid were added directly, and nitric acid alone was run in until the oxidation was complete. The solution was allowed to cool before fresh quantities of nitric acid, generally about 10 c.c., were added. With this amount of sulphuric acid complete precipitation always took place by adding 30 c.c. of 50 per cent ammonium nitrate to the oxidized residue made up to 150 c.c. with water.

The chief difficulty encountered in practice is the filtration and washing of the ammonium phospho-molybdate precipitate. A speedy method was found by the use of a special filtering tube. This consists of a glass tube about 8 cms. long and 2 to 2·5 cms. in diameter ; at one end a perforated platinum plate is sealed into it, and at this point the tube is drawn out to resemble an ordinary filter funnel. It thus combines the essential parts of a Buchner filtering funnel and a Soxhlet filtering tube. The plate is covered with either asbestos or filter paper.

By using this device filtration and washing of the precipitated phospho-molybdate can be completed in under five minutes. Ice-cold water for washing the precipitate, all of which is collected in the filter, is unnecessary. The precipitate is dissolved by alkali on the filter, and the solution run into the original flask, into which the remaining traces with the filter paper are washed with water.

It is advisable to avoid a great excess of ammonium molybdate, as a precipitation of molybdic acid may thus be brought about. Using 10 c.c. of acid potassium phosphate solution equivalent to 20 mg P_2O_5, the authors obtained 19·98 mg P_2O_5 as a mean of twelve experiments.

3. Isidore Bay [" Comp. rend.," 1908, **146**, 814].

This method is analogous to that described for sulphur by I. Bay.

The substance is burnt in a " bayonet " tube with magnesia and sodium carbonate (1 : 1), the product dissolved in dilute acetic acid, and the phosphate titrated against a solution of uranium nitrate (40 gms. to the litre), using potassium ferrocyanide as an indicator.

	Percentage phosphorus.	
	Carius.	Bay.
$(CH_3)_3P$	40·78	40·67
$(C_2H_5)_3P$	26·27	26·12

4. C. Marie [" Bull. Soc. Chim.," 1900, **23**, 44].

One gm. of the substance is dissolved in 15 to 20 c.c. concentrated nitric acid, the liquid gently heated, and finely divided potassium permanganate added in small portions until the liquid has acquired a permanent pink colour. Care must be taken at this point with substances not easily oxidized.

A 10 per cent alkali nitrite solution is now added to the cold solution until it becomes clear. Nitrous gases are expelled by boiling and the phosphoric acid precipitated with molybdate solution, care being taken to wash the precipitate free from manganese.

The analysis of glycero-phosphates is simplified by using this method of procedure.

Arsenic in Organic Compounds.

H. F. V. Little, E. Cahen, and G. T. Morgan ["Trans. Chem. Soc.," 1909, 1477].

Older Methods.—1. Combustion of the substance mixed with soda-lime by heating in a stream of air or oxygen. The residue is dissolved in hydrochloric or nitric acid, and the arsenic precipitated as sulphide. This latter is finally converted into magnesium pyroarsenate.—La Coste and Michaelis ["Ann.," 1880, 201, 224].

2. Pringsheim ["Amer. Chem. J.," 1904, 31, 386].

The organic derivative is oxidized by fusion with sodium peroxide, the arsenic being estimated gravimetrically as pyroarsenate. It has been pointed out that loss of volatile arsenic compounds may result on the use of high temperatures in this fusion.

3. Monthulé ["Ann. Chim. anal.," 1904, 9, 308].

The organic matter is destroyed by heating with nitric acid containing magnesium nitrate. A final ignition leads to the production of magnesium arsenate.

Proposed Method.—After a long series of experiments, the authors arrive at the conclusion that with due care in mixing and heating the reagents, the loss suggested in method 2 above becomes almost inappreciable, even when the oxidation is violent and the organic body somewhat volatile.

The chief difficulty found was the precipitation of magnesium ammonium arsenate in the presence of excess of alkali salt. Satisfactory results were obtained by dissolving the precipitate (which in every case was too high) and reprecipitating with ammonia.

Procedure.—The final method adopted introduced a volumetric determination due to Gooch and Browning ["Amer. J. Sci.," 1890 [iii.] 40, 66].

$$As_2O_5 + 4HI \rightleftharpoons As_2O_3 + 2H_2O + 2I_2.$$

Gooch and Browning have shown that the change takes place quantitatively from left to right when the liberated iodine is removed by boiling. The arsenious oxide is titrated with standard iodine.

The finely powdered substance (0·2 to 0·3 gm.) is mixed in a nickel crucible with 10-15 gms. of sodium peroxide and sodium carbonate in equal proportions, a portion being spread over the mixture to prevent loss by projection. A gentle heat is applied for about 15 minutes, and the fusion completed by raising the temperature to dull redness for 5 minutes.

The contents of the crucible are extracted with water and rinsed into a 450 c.c. conical flask. From 25 to 31 c.c. of sulphuric acid (1 : 1) are added cautiously, and, if necessary, the solution is boiled down to 100 c.c., when 1 gm. of KI is introduced and the liquid further concentrated to 40 c.c. A few drops of dilute sulphurous acid are added to destroy the last traces of iodine, and the bright green coloured solution is diluted considerably with hot water and saturated with hydrogen sulphide.

The arsenious sulphide is collected, washed about three times with hot water, dissolved off the filter with 20 c.c. of $\frac{N}{2}$ sodium hydroxide and the filtrate returned to the conical flask, where it is treated with 30 c.c. of hydrogen peroxide (20 volumes), the excess being destroyed by heating for 10 minutes on a water bath.

After frothing has subsided, a few drops of phenolphthalein are added, followed by 11 c.c. of sulphuric acid (1 : 1), this quantity giving 10 c.c. in excess. One gm. of KI is now added to the liquid, which should have a volume of 100 c.c., and the solution concentrated to 40 c.c., when its pale yellow colour is removed by a few drops of dilute sulphurous acid. Cold water is quickly added, and the diluted solution neutralized with 2N sodium hydroxide and just acidified with sulphuric acid. The requisite amount of 11 per cent sodium phosphate is added, and the arsenite solution titrated with standard iodine, using starch in the usual way.

Notes.—1. A gravimetric method may be used by pro-

ceeding as far as the oxidation of the sulphide with alkaline hydrogen peroxide and then precipitating as magnesium ammonium arsenate by the method of Austen ["Zeit. anorg. Chem.," 1900, **23**, 146].

2. The titration may be carried out in the presence of sodium hydrogen carbonate, but the addition of disodium hydrogen phosphate, advocated by E. Washburn, is preferable ["J. Amer. Chem. Soc.," 1908, **30**, 31].

The volume of 11 per cent sodium phosphate added should be equal to the number of c.c. of $\frac{N}{10}$ iodine required in the titration.

3. A substance containing little or no oxygen requires a proportionately larger amount of sodium peroxide.

4. Compounds containing iodine give rise on fusion to sodium iodate, which necessitates the addition to the acidified extract of sufficient sulphurous acid to reduce this salt to iodide, the reduction of the arsenate being then effected in the usual way.

Typical results :—

Atoxyl—As = 25·31 per cent calculated.
As = 25·07 to 25·46 per cent in 5 experiments.

Hexamethyl triaminotriphenylarsine—
As = 17·23 per cent (theoretical).
As = 16·98, 17·26, 17·20, 17·16 (found).

Triaminotriphenylarsine oxide—
As = 20·44 per cent (theoretical).
As = 20·57, 20·42 (found).

Toluene p-sulphonyl-p-aminophenylarsinic acid—
As = 20·22 S = 8·63 (theoretical).
As = 19·99, 19·73
S = 8·62 } (found).

Estimation of Antimony in Organic Compounds.

Fusion methods, as mentioned above in the case of arsenic, are usually employed. The antimony is finally precipitated by passing a stream of sulphuretted hydrogen and estimated in the usual manner.

CHAPTER III.

ESTIMATION OF TYPICAL GROUPS.

THE CARBOXYL GROUP.

Determination of the Molecular Weight of Acids.

The preparation and analysis of metallic salts of organic acids is the chief method in use for finding the molecular weight when the basicity is known, or *vice versâ*. The metallic salt used for this purpose depends on the nature of the compound. The silver salt is usually prepared, but some silver salts, such as silver oxalate, are explosive; others are very readily attacked by light. A preliminary test must be made first to ascertain the suitability of the silver salt, and if found unsuitable, either other metallic salts can be investigated or a different method employed.

Preparation and Analysis of a Silver Salt.—The acid or its aqueous solution is neutralized by ammonia and any excess of the latter boiled off. A solution of silver nitrate is added and the liquid cooled. Crystals of the sparingly soluble silver salt separate out and are collected and dried. Nearly all silver salts of organic acids crystallize without water of crystallization.

A weighed quantity of the silver salt is introduced into a porcelain crucible and gently heated. The organic matter is driven off and a residue of metallic silver remains. This must not be heated too strongly, because silver volatilizes at a somewhat low temperature. From the weight of silver remaining, and the basicity of the acid, the molecular weight can be calculated, e.g. if the acid is monobasic :—

$$R \cdot COOAg \rightarrow Ag.$$

Let x = weight of silver salt taken,
and y = ,, ,, ,, left,

then 108 gms. of silver come from $108\frac{x}{y}$ gms. silver salt.

$$\text{Molecular weight of acid} = (108\frac{x}{y} - 107).$$

In cases where the employment of the silver salt is not allowable, the calcium salt may be used, if convenient. The ignition must here be carried out at a high temperature in order to completely transform the $CaCO_3$ first formed to CaO.

Fifty-six gms. CaO are obtained from 1 gm.-molecule of the calcium salt of a monobasic acid.

If the sodium or potassium salt of the acid is available, a known weight is gently heated to drive off the organic matter, leaving a residue of pure carbonate in the crucible. This is treated carefully with a few drops of concentrated H_2SO_4, and heated gently from the upper part of the crucible slowly downwards. After cooling, it is treated again with a little acid, reheated and recooled. From the weight of alkali sulphate obtained, the molecular weight of the alkali salt, and therefore of the acid itself, is very simply calculated when its basicity is known. Barium salts may be similarly employed, in which case the estimation is carried out by precipitating as $BaSO_4$ in the general way.

If the molecular weight of an acid is known, its basicity can be got by direct titration against $\frac{N}{10}$ $Ba(OH)_2$, provided the acid is soluble in water.

Preparation and Use of Standard Baryta Solution.—A 3-litre flask, nearly full of distilled water, is brought nearly to boiling and pure crystalline $Ba(OH)_2 \cdot 8H_2O$ added till a saturated solution is obtained. This will be cloudy owing to the unavoidable presence of $BaCO_3$. The flask should therefore be closed by a rubber stopper carrying (*a*) a long tube reaching nearly to the bottom of the flask, and (*b*) a bent

soda-lime tube to cut off atmospheric CO_2. On cooling, the solution will become perfectly clear owing to the formation of a large mass of crystals of baryta which bring down all the $BaCO_3$. The clear solution, diluted if necessary, is syphoned off into the bottle A (Fig. 18), from which the burette B is filled by opening the tap D, access to CO_2 being prevented by the soda-lime tube C.

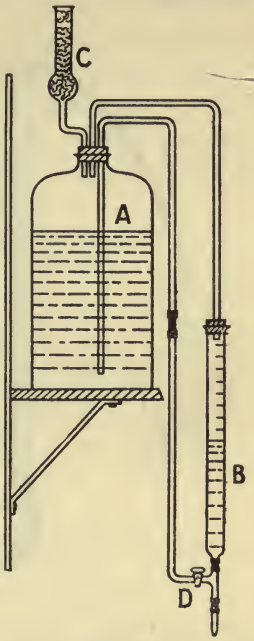


Fig. 18.

$\frac{N}{10}$ aqueous and alcoholic KOH are often used in titrating organic acids. In all cases phenolphthalein is the best indicator.

In addition to the direct methods there are several of an indirect nature in use for determining basicity and for estimation. The chief of these will now be described.

The Iodine-Oxygen Method.

Kux ["Zeit. anal. Chem.," 32, 129 (1893)].

A reaction which is common to all acids is the liberation of iodine from a mixture of KI and KIO_3. In the case of organic acids, representing the acid by R·COOH, the reaction goes quantitatively according to the equation:—

$$6R \cdot COOH + 5KI + KIO_3 = 6R \cdot COOK + 3I_2 + 3H_2O.$$

The liberated iodine can be most readily estimated by measuring the volume of oxygen evolved from an alkaline solution of H_2O_2:—

$$I_2 + 2KOH + H_2O_2 = 2KI + 2H_2O + O_2.$$

The volume of oxygen evolved, therefore, represents the volume of hydrogen replaced by potassium.

For ordinary work the apparatus shown in Fig. 19 suffices. It consists of a decomposition vessel A, inside which is fixed

a small cylinder B of 10-20 c.c. capacity. A is provided with a ground-in stopper, having a cock C. Connexion is made to an ordinary Lunge nitrometer by means of rubber tubing.

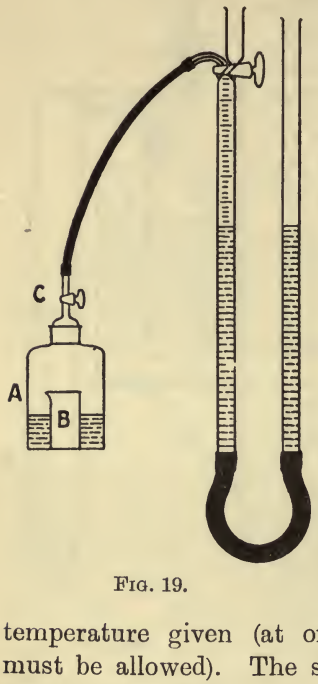


Fig. 19.

The reagents required are—

KI and KIO_3 both acid free.

H_2O_2 a 2 to 3 per cent solution.

Solution of KOH (1 : 1) which must be free from carbonate.

Boiled out distilled water free from CO_2.

To a solution of 0·1 to 0·2 gm. of the acid in 40 c.c. water 2 gms. KI and 0·2 gm. KIO_3 are added and the whole warmed for half an hour at 70° to 80°. Various acids require different times for completion of reaction, but the above is usually sufficient at the temperature given (at ordinary temperature twelve hours must be allowed). The solution is cooled and washed into the outer vessel A.

Into the inner vessel B is put a freshly-made and cooled mixture of 2 c.c. H_2O_2 solution and 4 c.c. KOH (1 : 1). The stopper is inserted and the Lunge nitrometer filled with water at atmospheric temperature. The levels in the two tubes are brought together at the zero mark and kept there. The cock C is opened and connexion made to the nitrometer. The water in the nitrometer will fall slightly; the levels are again adjusted. When no further movement of the water occurs it may be assumed that the apparatus is at constant temperature. The reading at atmospheric pressure is taken and then the vessel A is given a rotatory movement and gradually tipped on one side to mix the contents of A and B. The gentle shaking is continued till the level of the water remains constant. The pressure on the gas should be kept as near atmospheric as possible by lowering the open tube of the

nitrometer as fast as the gas enters. The level at atmospheric pressure is again read, and the difference gives the volume of oxygen evolved at atmospheric temperature and a pressure measured by the difference between the barometric height and the pressure of aqueous vapour at the room temperature.

It is advisable, where possible, to obtain an approximate value of the acid by titration and then to take a weight which will give a volume of oxygen of about 50 c.c.

In the original memoir the decomposition vessel and the measuring apparatus are both surrounded by water in order to secure constancy of temperature. The reaction, however, is over so quickly (15-20 secs.) that fluctuations of temperature in the modified apparatus are without appreciable influence.

The Carbonate Method.

Goldschmiedt and Hemmelmayr ["Monats.," 14, 210 (1893)].

0·5 to 1·0 gm. of the acid is introduced into the flask (Fig. 20), with 40 c.c. water. The stem of the dropping funnel is likewise filled with water. The CO_2 is passed through a Geissler tube containing concentrated H_2SO_4, which absorbs some water and shows the rate at which gas is passing through the tubes. Two $CaCl_2$ tubes are inserted to absorb all moisture, and then the CO_2 is absorbed in the stoppered soda lime tube. This last is protected by a small $CaCl_2$ tube connected to an aspirator.

A stream of CO_2-free air is drawn slowly through the liquid, which is kept gently boiling. A weak suspension of $BaCO_3$ in boiling water is run in from the tap funnel in small quantities at a time. The CO_2 evolved is freed from water by H_2SO_4 and $CaCl_2$ (one tube of which is probably sufficient) and absorbed in the soda lime tube. The increase in weight of this tube gives the weight of CO_2 evolved from the weight of acid taken :—

$$2\,R.COOH + BaCO_3 = (R.COO)_2\,Ba + CO_2 + H_2O.$$

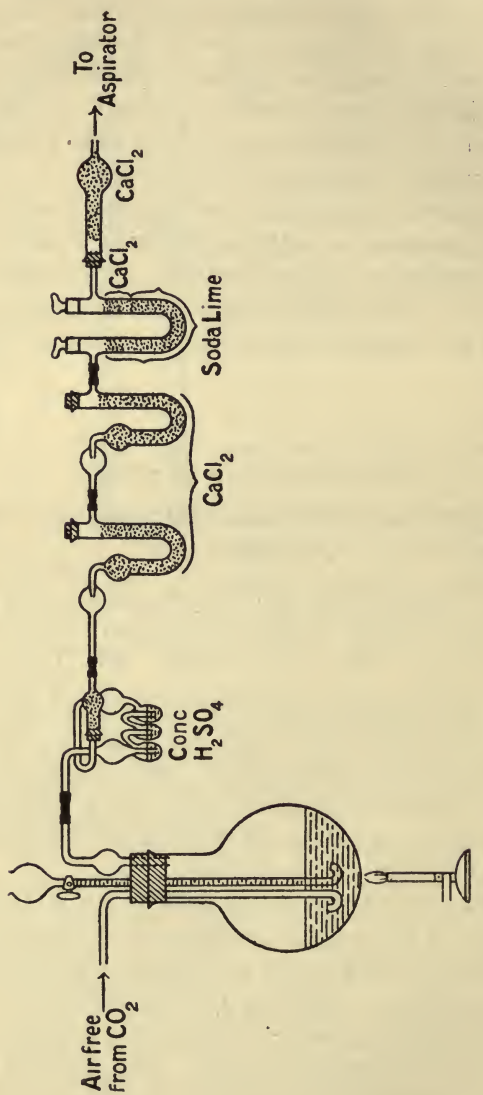

Air free from CO_2
Conc H_2SO_4
$CaCl_2$
Soda Lime
$CaCl_2$
$CaCl_2$
To Aspirator

FIG. 20.

Hydrogen-Sulphide Method.

F. Fuchs ["Monats.," 9, 1132, 1143 (1888)].

This method was devised for obtaining the basicity of those acids to which the silver salt method cannot be successfully applied.

Alkali hydrosulphide attacks acids with evolution of sulphuretted hydrogen :—

$$NaHS + R.COOH = R.COONa + H_2S.$$

Every volume of replaceable hydrogen gives rise to two volumes of sulphuretted hydrogen.

For quantitative success the action must be carried out in an atmosphere of H_2S which is kept constant during the experiment, and since the time is so short (2 to 5 mins.) this does not present much difficulty.

The excess of H_2S is estimated either (*a*) volumetrically or (*b*) by the amount of air which it displaces.

Preparation of NaHS Solution.—A solution of commercial NaOH containing 1 part in at least 10 of water (many sodium salts of organic acids are difficultly soluble in NaHS) is boiled with a few c.c. of $Ba(OH)_2$ solution in order to precipitate carbonates. This liquid is allowed to cool and settle, and the clear liquid poured off into a flask kept in cold water. Into the flask pure H_2S is led, and the passing of gas continued 2 to 3 minutes after absorption has ceased.

(*a*) *Volumetric Method.*—A small Erlenmeyer flask may be used for the estimation (see Fig. 21), provided with a rubber bung pierced with two holes, one for a delivery tube of capillary bore, and the other for a glass rod and the neck of the bottle containing a weighed amount of the acid under investigation. This weighing bottle can be readily made from a small test tube, which is drawn out about 1-1½ cms. from the closed end to a diameter of 3 mm. In the centre of the small bulb thus formed, a hole is blown, and then the piece is cut off at the constriction. The bulb should then appear of form shown in Fig. 22.

The finely powdered acid (·05 gm.) is weighed into this, and it is then pushed into the hole in the cork to, say, 3 mm. from the under side. From the top a glass rod of

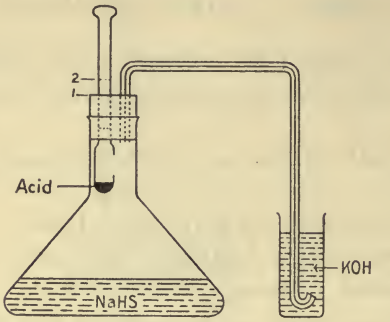


FIG. 21.

FIG. 22.

equal diameter to that of the tube is pushed, so that its bottom edge just touches the top of the weighing tube. A mark is made on the rod level with the top of the cork—mark 1; and another mark—mark 2—is made above this equal to the length of neck of bottle inside cork, in this case 3 mm.

Thirty c.c. of the NaHS solution are placed in the flask together with 0·25 gm. of oxalic or tartaric acid. The cork and fittings are adjusted in position. H_2S is evolved and displaces the air from the apparatus. When the gas evolution ceases, a small long and narrow beaker full of conc. KOH is placed under the delivery tube. Since KOH absorbs H_2S the liquid rises in the delivery tube. The glass rod is now pushed into the cork up to mark 2 and the level of the liquid in the delivery tube noticed. H_2S is now evolved and is absorbed by the KOH. When the action ceases, the level of the liquid in the capillary delivery tube is brought to that immediately before the experiment and the KOH beaker removed.

The alkali is diluted to about 500 c.c., neutralized with acetic acid, and titrated with standard iodine, using starch as indicator :—

$$H_2S + I_2 = 2HI + S.$$

The error caused by the displacement of H_2S when the rod is pushed from the mark 1 to mark 2 is negligible.

(*b*) *Estimation by Measurement of Displaced Air.*—It should theoretically be possible to estimate the H_2S evolved by collecting over mercury, since any action of H_2S on mercury would give rise to an equal volume of hydrogen.

$$Hg + H_2S = HgS + H_2$$
$$2Hg + H_2S = Hg_2S + H_2.$$

The procedure employed by Fuchs, however, was to liberate H_2S as in the first method, and to cause it to displace a long column of air contained in a long bent delivery tube (to prevent diffusion), and to collect and measure this air.

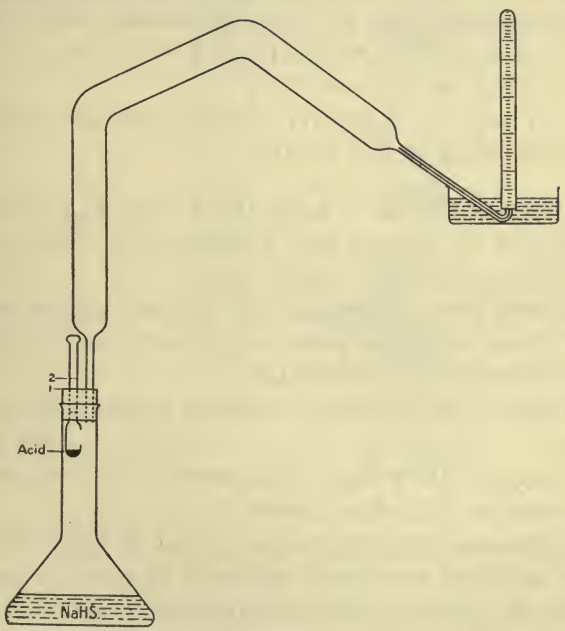


FIG. 23.

A long-necked conical flask was used (Fig. 23) with the same fittings as before except that the delivery tube was of wide bore, sealed to a narrow glass tube in the cork, and to a capillary tube for the delivery of displaced air to the measuring tube.

The flask is filled with H_2S as before, and dry air fills the delivery tube. The cork is inserted, the capillary tube placed under water, and the measuring tube full of water put in position. After 1 minute the glass rod is pushed from mark 1 to mark 2, and the tube and acid fall into the NaHS solution. The H_2S evolved forces air from the delivery tube into the measuring cylinder. When the evolution of air ceases the measuring tube is transferred to a cylinder of water, the pressures equalized, and the volume reduced to N.T.P.

Every gm.-molecule of a monobasic acid liberates 22·4 litres of H_2S at N.T.P.

Note.—A mixture of H_2S and air fills the lower end of the delivery tube, but no H_2S gets into the measuring tube. A second experiment can be done immediately after the first with the same solution of NaHS, but the delivery tube must first be washed out with *dry* air.

The hydrogen of hydroxyl groups in alcohols and phenols is not replaceable by this reaction.

An improved form of apparatus for the H_2S method has been devised by Hunter and Edwards ["J. Amer. Chem. Soc." (1913), 35, 452].

The chief sources of error in the original apparatus are :—

1. Failure to obtain perfect equilibrium in the saturation of the alkaline solution with H_2S.
2. Inability to tell when constant temperature has been attained.
3. Change in the volume of the gas due to the back pressure of the water in the delivery tube.
4. Convection currents carrying some H_2S into the water.

The modified apparatus, designed to avoid these errors, is shown in Fig. 24. The decomposition is effected in the small bottle D, which is fitted with a three-holed cork carrying (*a*) an entry tube (with stop tap) for H_2S, which is made by passing the gas from H_2SO_4 and FeS into KOH and decomposing this solution with acid; (*b*) a T-tube having its side limb connected to a rod, on which rests the tube containing the weighed amount of acid, the arrangement being similar to that employed in the V. Meyer vapour density

apparatus : the open limb of the T-piece is closed by a rubber stopper ; (*c*) a wider glass tube leading just into the air chamber E, and provided at A with a 3-way tap connecting D, E, and the atmosphere ; the rubber and pinch-cock are present as a safeguard in case the neutral position of the 3-way tap is untrustworthy.

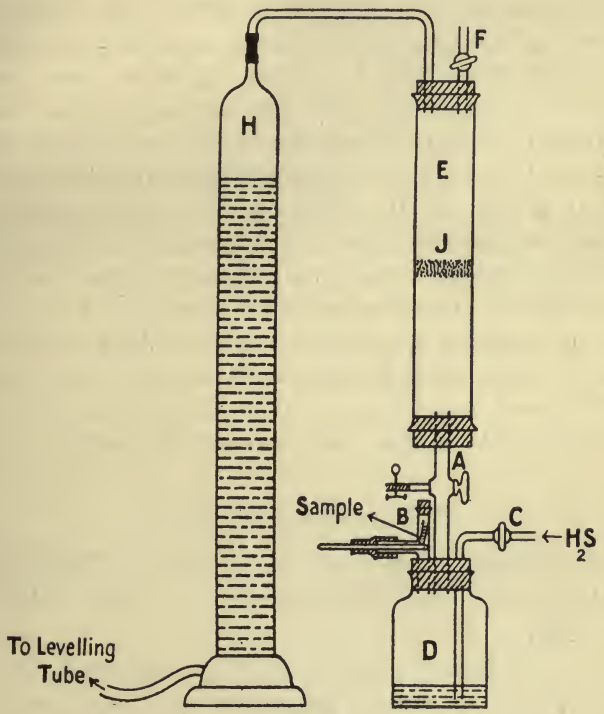


FIG. 24.

A loose plug of cotton wool, J, is placed near the middle of the air chamber, E, whose upper cork carries a delivery tube to the measuring limb of a Hempel burette, H, and also a small glass tube provided with a tap at F.

Having set up the apparatus (minus the sample), the tube E is dried by passing a stream of dry air through it for five minutes from A to F.

Twenty-five c.c. of 10 per cent KOH, free from K_2CO_3, are put into D and a stream of H_2S passed from C through A into

the atmosphere, keeping E rigidly shut off. The pinch-cock on the side tube of A is now closed, and the cork of the sample holder removed, H_2S still passing. The tube containing the weighed sample is placed on the rod and the cork reinserted. When the H_2S ceases to bubble through the solution D is shaken for five minutes. The pinch-cock of A is reopened and the solution in D again shaken for three minutes with H_2S coming through. The stream of gas is then slowed down and the apparatus allowed to stand for half an hour to come to the air temperature. The gas burette is connected to E and levelled at about 99 c.c., the H_2S is cut off by closing C, and D and E are put into communication, and the level again read. D is then gently shaken for two minutes; no difference in level greater than 0·1 c.c. should occur. Having accurately determined this level the sample is allowed to drop into the liquid. The pressure in the apparatus is kept atmospheric by lowering the levelling tube. When no more gas comes off, D is shaken for three minutes and the volume read. The difference in readings gives the volume of H_2S evolved, this is reduced to N.T.P., and calculated to (COOH).

The Ammonia Method.

This method is based on the method of McIlhiney for ascertaining the saponification value of dark-coloured fats (see p. 187).

The procedure is exactly as there described after the saponification. It gives good results with weak acids, and is convenient for discoloured acids where direct titration is impossible.

ESTERS.

Hydrolysis of Esters by Alcoholic KOH.

Preparation of Alcoholic KOH of Approximately $\frac{N}{2}$ *Strength.*—The following two methods have been described; the second is the one usually adopted in practice:—

(*a*) 5-6 gms. fused KOH are dissolved in 5 c.c. water and diluted with absolute alcohol to 200 c.c. This solution is clarified by agitation with 5 gms. Na_2SO_4, and the clear solution poured off and standardized with hydrochloric acid, using phenolphthalein as indicator.

(*b*) 30 gms. stick KOH are dissolved in 1 litre of 95 per cent alcohol in the cold, and left at atmospheric temperature until solution is effected, the bottle being well shaken. The clear liquid is syphoned off into a stoppered bottle and exposed to diffused daylight. It is thus bleached and can be kept for some time unchanged in diffused light. It is then standardized as in (*a*).

Hydrolysis of the Ester or its Alcoholic Solution.—The ester is weighed out in one or other of the three following ways:—

(1) In an ordinary weighing-bottle, if non-volatile, and poured into the hydrolysis flask, the bottle washed with absolute alcohol and the washings added.

(2) In a short glass tube provided with a cover (Fig. 25). This can be readily made by cracking off two ignition tubes (one slightly larger in diameter than the other), by making a file mark and applying a hot glass rod to this mark, when the tube usually cracks right round quite evenly.

Fig. 25.

The cap is removed before dropping it into the hydrolysis flask.

(3) In a thin bulb drawn into a capillary (Fig. 26). This is made from a piece of ordinary soft glass tubing, by drawing out in two parts so as to get a tube of the form shown in Fig. 27.

Fig. 26.

The glass is cracked at *a* and this end sealed. The bulb

portion *b* is heated up strongly and blown into a thin bulb. The bulb is weighed and then inverted so that the capillary tube is under the liquid. By warming the bulb air is driven out and liquid enters. When sufficient liquid has been thus introduced, the capillary is sealed off and allowed to cool. It is then reweighed.

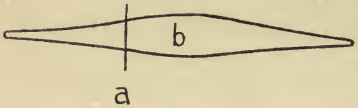


FIG. 27.

This bulb is dropped into the reaction flask, and when all is ready may be easily broken (if made thin) against the sides of the flask.

The reaction flask is of about 300 c.c. capacity and is fitted with a ground-in air condenser. 50 c.c. of alcoholic KOH are put in, and a known weight of ester (about 3 gms.) introduced. The condenser is immediately attached, and the flask is heated up on a water bath for two hours.

$$R \cdot COOR_1 + KOH = R \cdot COOK + R_1OH.$$

A little water is run down the condenser and the contents of the flask titrated against standard HCl.

From the weight of KOH required to hydrolyze the ester the percentage of the latter is readily got, the calculation presenting no difficulty.

THE AMIDO GROUP.

Amides are estimated by hydrolysis with alkalis (KOH, $Mg(OH)_2$, $Ba(OH)_2$, etc.) or with sulphuric acid. In the former case the ammonia is driven over directly into standard acid and the excess titrated. In the latter case the ammonia is liberated from the ammonium sulphate by excess of alkali and distilled over just as in the Kjeldahl method of estimation of nitrogen, page 46.

The velocity of hydrolysis of amides has been studied by Remsen and Reid, "Amer. Chem. J.," 21, 284 (1899); Reid, "Amer. Chem. J.," 24, 397 (1900); Lutz, "Ber.," 35, 4375 (1902).

Effront ("Ber." (1904), 37, 4290) has applied the hypochlorite reaction to amides, but instead of measuring the N

evolved, he estimates the available chlorine used up. Preliminary experiments showed :—

(1) An alkaline hypochlorite solution is stable in absence of air.

(2) Amines, imines, nitriles, acid amides and amino-acids react with hypochlorite in the cold, using up an amount of available chlorine directly proportional to the weight of substance employed.

(3) Ammonium bases do not react at ordinary temperature.

1 to 5 c.c. of a 1 per cent solution of the substance, together with 20 c.c. of a calcium hypochlorite solution (1·5 to 2 per cent available chlorine), and 20 c.c. N . NaOH, are brought into a 50 c.c. flask, which is then filled to the mark with water. After standing 12 to 15 hours the contents are titrated against a standard solution of arsenious acid. Urea requires 1·77 gms. Cl for each gm.

$$\underbrace{CO(NH_2)_2}_{60} + \underbrace{3Cl_2}_{106{\cdot}5} + H_2O = CO_2 + 6HCl + N_2.$$

THE ACETYL GROUP.

Perkin's Method.

A. G. Perkin ["J. C. S." (1905), **87**, 107].

This depends on the formation of ethyl acetate by the interaction of the acetyl compound and ethyl alcohol in the presence of conc. H_2SO_4 :—

$$R . O . COCH_3 + C_2H_5OH = R . OH + CH_3 CO . O . C_2H_5.$$

A 200 c.c. distilling flask is placed on a gauze in an inclined position (Fig. 28), and its side tube bent to fit a long water condenser, whose open end leads into a hydrolysis flask, containing 25 c.c. $\frac{N}{2}$ alcoholic KOH, to which a reflux condenser can afterwards be fitted.

The distilling flask is provided with a dropping funnel with its stem about 3 in. above the bottom of the flask. 0·5 gm. of the acetyl compound with 30 c.c. of pure alcohol and

3 c.c. conc. H_2SO_4 are introduced into this flask and gently distilled, a few pieces of porous tile being put in to avoid

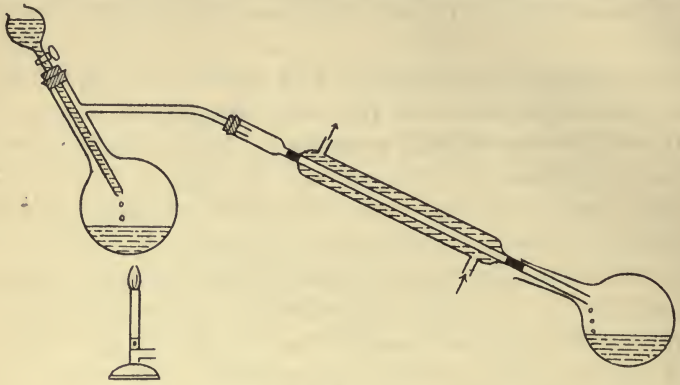


Fig. 28.

bumping. From the dropping funnel 20 c.c. of pure alcohol are run in at a rate corresponding to that at which the liquid distils over. The distillation proceeds, and another 20 c.c. alcohol are run in as before (sometimes even a third addition being necessary). The distillation should be continued until the bulk of liquid in the flask is only about one-third of the original. The receiving flask is fitted with a reflux water condenser and heated on the water bath for half an hour, diluted with a little water and titrated with $\frac{N}{2}$ H_2SO_4 using phenolphthalein as indicator.

The distillation should not be too rapid or carried too far, otherwise SO_2 may be produced and vitiate the titrations.

O-acetyl compounds generally go readily, but N-acetyl compounds require repeated treatment with alcohol, owing to their greater resistance to hydrolysis.

Wenzel's Method.

["Monats.," 18, 659 (1897)].

The special features here introduced are :—

(*a*) Flask of beads as a trap for phosphoric acid.

(*b*) Distillation in vacuo.

A stout 300 c.c. distilling flask A is used for hydrolysis (Fig. 29). It is fitted with a two-holed rubber stopper;

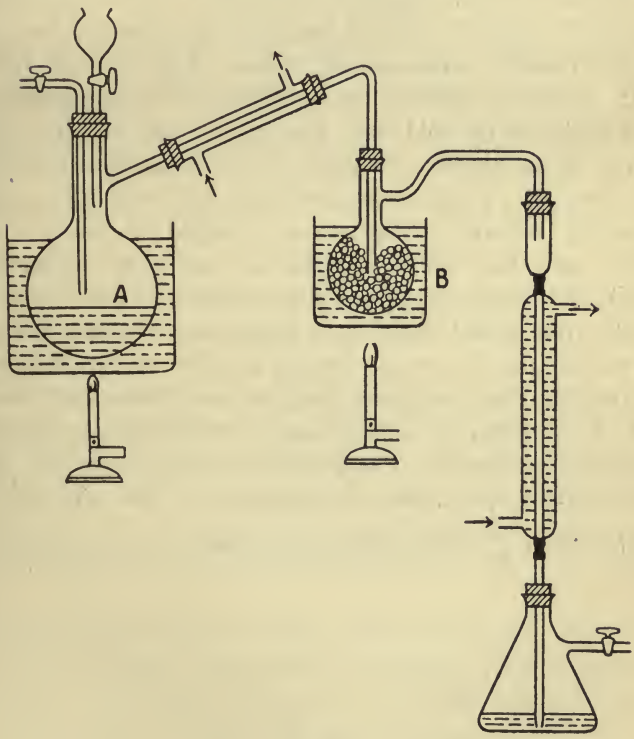


Fig. 29.

through one hole enters a thick walled narrow tube from a hydrogen generator. This tube is provided with a glass tap. Through the other hole comes a tap funnel drawn out at its lower end, which reaches about 2 cms. below the side tube. This side tube is bent upwards and is surrounded by

a small water condenser; it leads to the middle of the bulb of a second stout distilling flask B of about 100 c.c. capacity filled with glass beads. This serves to catch any phosphoric acid distilling over. The side tube of B passes into a water condenser arranged vertically in a pressure flask, which contains a known volume (excess) of standard KOH solution. The exit tube of the pressure flask is connected to a good water pump.

0·2 to 0·4 gm. of the acetyl compound with 3 c.c. H_2SO_4 (2 : 1) and 3 c.c. water is put into A. The apparatus is exhausted, and A and B warmed by heating the water in the beakers surrounding them. After about half an hour hydrolysis should be complete. The hot water from A is replaced by cold and the pump shut off (but not of course to let air in). Twenty c.c. of a solution containing, per litre, 100 gms. metaphosphoric acid and 450 gms. dihydrogen sodium phosphate are added through the tap funnel and the whole distilled in vacuo to dryness, the distillation being continued for a further 10 minutes.

The hot water under A is again removed, the pump cut off, and 20 c.c. of air-free boiling water run into A from the tap funnel. This is again distilled to dryness and serves to wash the apparatus. The pump is cut off and the apparatus filled with hydrogen. The condenser is then detached, rinsed with a little water, and the contents of the pressure flask titrated with $\frac{N}{10}$ acid using phenolphthalein as indicator.

Hydrolysis with Alcoholic KOH.

R. and H. Meyer ["Ber." (1895), **28**, 2965].

R. Meyer and E. Hartmann ["Ber." (1905), **38**, 3956].

0·5 gm. of the substance is heated under a reflux condenser with 5 gms. NaOH and 50 c.c. of methyl alcohol (which has been distilled over K_2CO_3), for one hour. The solution is cooled and acidified with 50 c.c. phosphoric acid, sp. gr. 1·104. The whole is distilled in steam till the distillate is no longer acid, when it is titrated against $\frac{N}{10}$ $Ba(OH)_2$ using phenolphthalein as indicator.

Hydrolysis with Benzene-Sulphonic Acid.

Sudborough and Thomas ["J. C. S." (1905), **87**, 1752].

The sulphonic organic acids, e.g. those of benzene and naphthalene, have the advantage of being stronger acids than H_3PO_4, and they do not give off SO_2 or any other gas during the hydrolysis.

Preparation of Benzene Sulphonic Acid.—Kahlbaum's barium benzene sulphonate is distilled in steam till the distillate is neutral. This gets rid of small amounts of volatile acid impurities. The hot solution is then mixed with the theoretical amount of sulphuric acid and filtered, the filtrate being made up to a convenient strength, e.g. 15 or 20 per cent.

Estimation.—A known weight of the acetyl compound is mixed with an excess of the benzene sulphonic acid solution and distilled. When the residue in the flask becomes too concentrated, distilled water is added, and the operation continued until the distillate is neutral. The distillate is titrated with standard $Ba(OH)_2$, using phenolphthalein as indicator. The apparatus in Fig. 28 serves well for this method.

THE HYDROXYL GROUP.

Acetylation of (OH) Groups.

(*a*) *By Acetic Anhydride.*—Verley and Bölsing ["Ber." (1901), 34, 3354].

Acetylation by acetic anhydride in the cold is a slow process, but it may be considerably hastened by the addition of pyridine and warming on the water bath for a short time.

$$R.OH + (CH_3CO)_2O + \text{Pyridine} =$$
$$R.O.CO.CH_3 + CH_3.COOH : \text{Pyridine}.$$

Since the acetic acid formed is at once taken up by the pyridine it can exert no hydrolyzing influence on the acetyl compound. The amount of acetic acid thus taken up is determined by titration with alkali, which decomposes the pyridine salt forming sodium acetate. The details for quantitative work are as follows :—

A mixture of 120 gms. acetic anhydride and 880 gms. of pyridine is used for acetylation. Twenty-five c.c. are equivalent to 60 c.c. N. alkali.

1 to 2 gms. of the hydroxy compound are weighed into a 200 c.c. flask, 25 c.c. of the pyridine solution added, and the flask heated on a water bath for a quarter of an hour. A condenser is unnecessary as direct experiment has shown that no anhydride is lost by evaporation. The mixture is cooled, 25 c.c. of water added, and titrated against standard alkali, using phenolphthalein as indicator.

The exact value of the acetic anhydride solution is got by decomposing with water and titrating as before. From the value of the acetic acid found, the amount of (OH) is easily deduced from the equation given.

The method gives good results in most cases, and is applicable to many phenolic compounds.

(*b*) *By Acetyl Chloride.*—F. Adam ["Öst. Chem. Ztg.," 2, 241].

The alcohol is treated with acetyl chloride and the excess decomposed by water giving both acetic acid and hydrochloric acid.

$$\left.\begin{array}{l} CH_3.CO.Cl + R.OH = R.O.CO.CH_3 + HCl \\ CH_3.CO.Cl + H.OH = CH_3.COOH + HCl \end{array}\right\}$$

By titrating the total acid at the end of the experiment the amount of (OH) can be calculated from these two equations, e.g. 1 c.c. N. NaOH $\equiv$ 0·0880 gm. amyl alcohol.

One to two gms. of the substance are weighed into a dry 250 c.c. flask and 10 to 25 c.c. of a 5 to 10 per cent solution of acetyl chloride in chloroform run in from a tap burette. The flask is fitted with a cork carrying a 100 c.c. tap funnel, or, better, a flask having such a funnel fused into its neck is used. The tube of this funnel is filled with water. After standing for about 2 hours the acetylation is complete. A Varrentrapp absorption apparatus is fitted to the mouth of the tap funnel and partly filled with water. About half the water in the funnel is allowed to run into the flask and the displaced air bubbles up through the water, both in the funnel and in the absorption apparatus, and is there deprived of any acid vapour it may contain. The flask is then well shaken and the remainder of the water run in and again shaken. By tilting, the water from the absorption apparatus flows into the funnel, and so into the flask, and a little fresh water is put in to rinse out these parts, the cork being raised to allow an easy flow. The contents of the flask are titrated against N. or $\frac{N}{2}$ alkali, using phenolphthalein as indicator.

The titre of the acetyl chloride solution is got in a similar way by decomposing with 100 c.c. of water, and from the difference the amount of (OH) or of alcohol is got from the equations given above.

This method gives good results with ethyl and amyl alcohols, and can be used for the estimation of fusel oil in brandy and for the alcohol number of ethereal oils.

Application of Grignard Reagent.

Sudborough and Hibbert ["J. C. S." (1904), p. 933].

The Grignard reagent reacts with the hydroxyl group liberating a paraffin. In the case of methyl magnesium iodide, the reaction takes the following course:—

$$R . OH + CH_3MgI = RO . MgI + CH_4$$

As is well known this reaction requires the presence of a catalyst, and for this purpose the ethers are usually employed. In this case pure amyl ether is used.

Purification of Amyl Ether.—Ordinary amyl ether is dried over $CaCl_2$ and boiled under a reflux condenser with metallic sodium. 15 c.c. of an ordinary amyl ether solution of CH_3MgI (see below) is added, together with a little fresh sodium, and the whole again boiled under a reflux condenser for 15 minutes. The liquid is then left for several hours over P_2O_5 and finally distilled, the distillate being kept away from any traces of moisture.

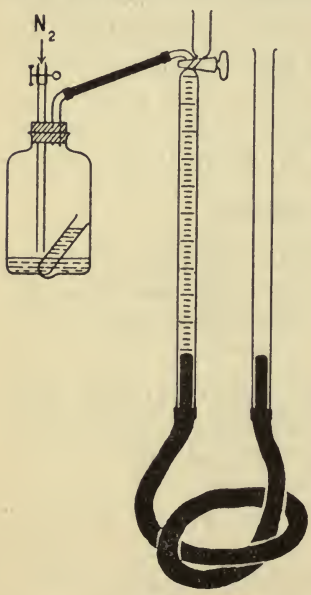


Fig. 30.

Preparation of Methyl Magnesium Iodide.—6·09 gms. dry magnesium turnings are added to 100 c.c. dry amyl ether, and 35·5 gms. of methyl iodide dissolved in 20 c.c. of the amyl ether, introduced. By gently warming on a sand bath a vigorous action ensues, and this is allowed to proceed at ordinary temperature and completed by heating for half an hour under a reflux condenser. The clear liquid is then decanted from the undissolved magnesium, made up to 200 c.c. with pure amyl ether, and kept well stoppered.

Estimation.—A dry 200 c.c. bottle (Fig. 30) is fitted with a rubber stopper carrying (*a*) a tube (with stopcock) reaching

nearly to the bottom of the bottle, (*b*) a short delivery tube leading to a Lunge nitrometer filled with dry mercury.

10 to 20 c.c. of dry amyl ether and 0·10 to 0·25 gm. of the substance are placed in the bottle, and an excess (15-20 c.c.) of the methyl magnesium iodide solution contained in a small tube is lowered into the bottle, so that no mixing of the two liquids will occur until all is ready. The air is now displaced from the bottle by a current of dry nitrogen, attachment made to the nitrometer and the whole allowed to attain constant temperature. The height of the mercury at atmospheric pressure is read off and then the two liquids in the bottle are mixed and shaken vigorously. The volume of methane evolved at N.T.P. is obtained from readings of the mercury level before and after mixing.

$$1 \text{ c.c. } CH_4 \equiv 0{\cdot}000759 \text{ gm. OH.}$$

Good results were obtained for *α*-naphthol, *β*-naphthol, resorcinol, pyrogallol, o-nitrophenol, benzoin, acetoxime, etc.; but see p. 107 for limitations of the method.

METHOXYL AND ETHOXYL GROUPS.

All the usual determinations of these groups are based on the original method of Zeisel which consists in decomposing the compound with hydriodic acid thus :—

$$R(OCH_3)_n + nHI = R(OH)_n + nCH_3I$$

the methyl iodide is led into alcoholic silver nitrate solution and the precipitated silver iodide is washed, filtered, and weighed.

Preparation of Hydriodic Acid (according to Hewitt).[1]— 3 gms. of red phosphorus and 35 gms. of iodine are put into the flask A (Fig. 31) which is provided with a dropping funnel and delivery tube, the latter connecting to a U-tube B lightly packed with asbestos or glass wool, dusted over with 3 to 4 gms. of red phosphorus. The exit tube of B enters the tubulure of a retort C whose neck dips beneath 30 gms. of water contained in the flask D. This retort prevents back suction of the liquid into the apparatus.

[1] "Methods of Organic Manipulation," by J. T. Hewitt (Whittaker & Co.).

12 to 15 gms. of water are dropped very slowly from the dropping funnel on to the mixture of phosphorus and iodine. At first a vigorous action ensues, which afterwards slows down, and is completed by heating the flask A.

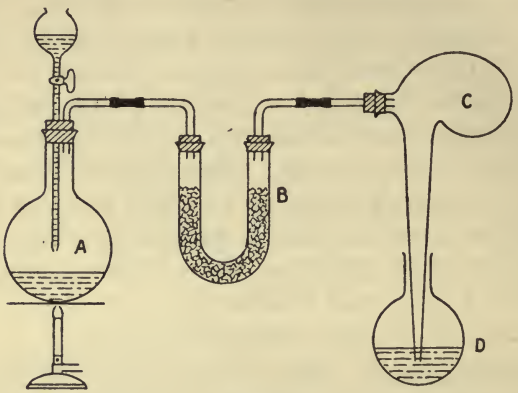


Fig. 31.

The solution of hydriodic acid is fractionally distilled until a fraction boiling constantly at 126° C. with sp. gr. 1·68 is obtained, and this is used for the estimations.

Alcoholic $AgNO_3$.—4 gms. of silver nitrate are dissolved in 10 gms. of water, the liquid cooled, and 90 c.c. of absolute alcohol added. The solution is well stoppered and kept in the dark.

Zeisel's Method.

["Monats.," **6**, 989 (1885); **7**, 406 (1886).]

The apparatus devised by Zeisel is shown in Fig. 32. Though now not often used it is important as showing the original method of fractionating the methyl iodide from the hydriodic acid. The developments since introduced will be mentioned later.

A small distilling flask A of about 50 c.c. capacity has its side tube bent almost horizontal and is placed in a glycerine bath. The neck of A is connected as shown to a long tube of $\frac{1}{4}$ in. bore passing through a wider tube, and fitted to it by corks which also carry an inlet and an outlet tube. This

arrangement serves as a fractionating condenser. The inner tube of the condenser leads to the potash bulbs B which contain water and ¼ to ½ gm. of red phosphorus, and are immersed in a water bath kept at 60° C. In C is placed 50 c.c. of alcoholic $AgNO_3$ and in D 25 c.c. of alcoholic $AgNO_3$.

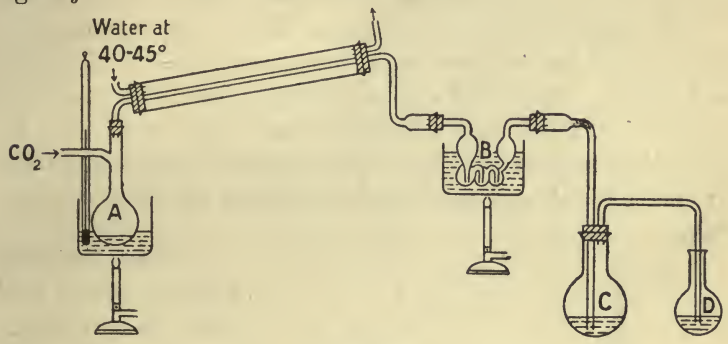


Fig. 32.

0·3 gm. of the methoxyl compound is introduced into A and covered with 10 c.c. of hydriodic acid sp. gr. 1·68. A slow stream (1 bubble per second) of washed CO_2 is passed continuously through the apparatus, and water at 40-45° circulated through the fractionating condenser. At this temperature the methyl iodide is allowed to distil over whilst the hydriodic acid is returned to the flask A. The glycerine bath under A is slowly raised to a temperature of 130° C., and the heating continued until the liquid in C is clear and the precipitate is settling well. This should be the case in about 2 hours. The liquid in C and D is decanted into a beaker of 500 c.c. capacity and the precipitate is further washed two or three times by decantation with a little water and the washings added to the bulk in the beaker. This process partly breaks up the double salt of silver iodide and silver nitrate which is formed, the latter being removed by the water. The residual precipitate is transferred to a small beaker, covered with dilute HNO_3 and allowed to stand. The washings are diluted to 300 c.c. and evaporated down till the alcohol has been removed; 2 to 3 c.c. HNO_3 are added towards the closing stage of the evaporation.

Both precipitates are now filtered off on the same paper, washed, dried, and weighed.

1 gm. AgI = 0·13202 gm. OCH_3.

Hewitt and Moore's Modification.

["J. C. S." (1902), **81**, 318.]

The method of fractionation of Zeisel's apparatus is very tedious and the first important modification is due to Hewitt and Moore. They used a fractionating column to separate the methyl iodide from the hydriodic acid and found that the method allowed them also to dispense with the Geissler tubes in the original apparatus, and to shorten the time of experiment.

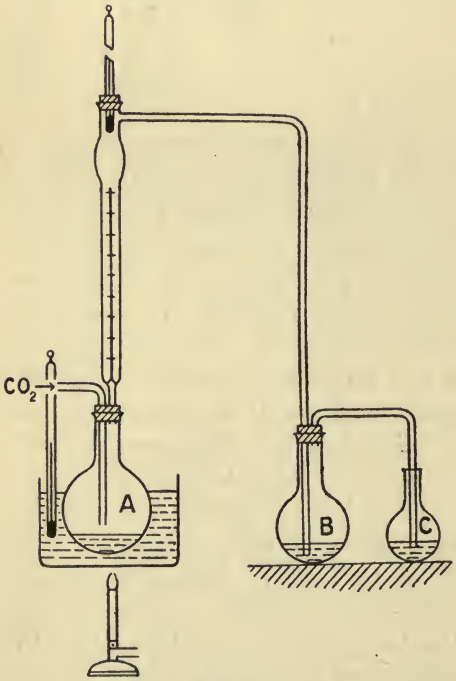


Fig. 33.

16 c.c. of hydriodic acid are placed in A which is of 200 c.c. capacity and is fitted with a cork, carrying a CO_2 entry tube (running to about 2 cms. above the liquid), and a rod and disc fractionating column. This flask A is heated by the glycerine bath. A slow current of CO_2 is passed through the apparatus for 10 minutes, and then 0·2 to 0·3 gm. of the substance is introduced into A. The apparatus is connected together and the glycerine bath warmed up to 130°. The CH_3I passes directly into B and C which contain respectively 50 and 25 c.c. of alcoholic $AgNO_3$ (p. 94). The thermometer at the

top of the fractionating column should indicate 20°-25° and the experiment should be completed in 40 minutes. The treatment of the precipitate is as recorded in Zeisel's method.

For ethoxyl compounds the glycerine bath is heated to 140° and the temperature at the top of the column should be about 27°. The current of CO_2 is increased towards the end of the experiment.

Perkin's Method.

["J. C. S." (1903), 83, 1367.]

A long-necked Wurtz flask is used to effect the fractionation. Originally Perkin used a neck of 16 ins. and also inserted a flask containing water and phosphorus between the distilling flask and the alcoholic $AgNO_3$, but later he found that not only could the latter be dispensed with, but that it was quite safe to shorten the neck of the flask to 8 in. His apparatus is given in Fig. 34.

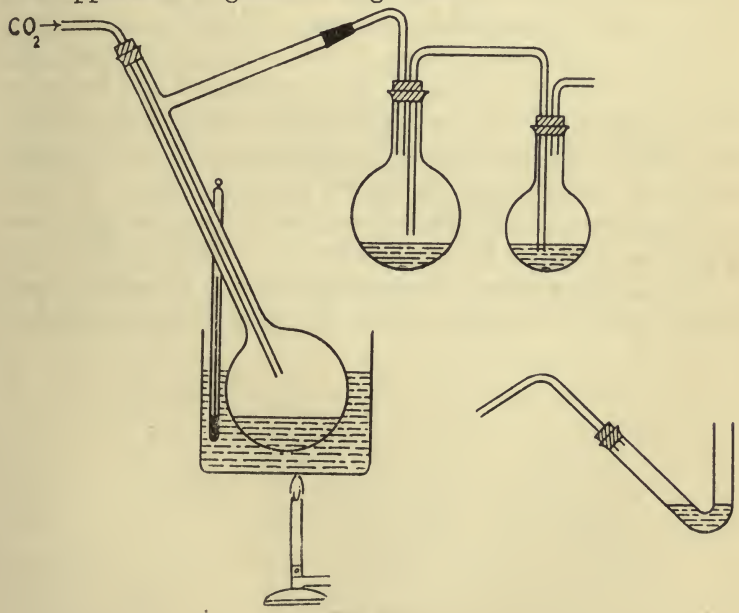


Fig. 34.

Through the cork of an 8 in.-necked Wurtz distilling flask passes a CO_2 entry tube reaching to near the surface of

the liquid. The side tube of the flask is connected to two flasks, the first containing 20 c.c. and the second 15 c.c. of alcoholic $AgNO_3$. The connecting tube between these two flasks acts as a syphon, dipping just below the liquid in the second flask and being just above the liquid in the first flask.

0·3 to 0·35 gm. of the substance is weighed into the decomposition flask and covered with 15 c.c. of hydriodic acid of sp. gr. 1·68. A slow current of CO_2 is forced through the apparatus and the glycerine bath raised to 130°-140°. When the liquid in the first $AgNO_3$ flask is fairly clear and the precipitate has settled well the temperature is raised till the hydriodic acid boils and it is kept thus for one hour. After that time the silver nitrate flasks are replaced by the V-tube containing a few c.c. of alcoholic $AgNO_3$ and the heating continued for 15 minutes longer. If no precipitate forms the operation may be taken as completed, but if a precipitate is produced the liquid in the V-tube is added to that in the second flask and replaced by fresh, the heating being continued for another 20 minutes, and so on till all the methoxyl body has been decomposed. The contents of the flasks are added gradually to 50 c.c. of boiling water acidified with HNO_3 and boiled until the alcohol has been driven off. The precipitate is allowed to settle, filtered and weighed.

The results with ethoxyl compounds are generally somewhat low, probably due to the reduction of EtI by HI.

In all cases where the decomposition is difficult it is advisable to help it by the addition of a little acetic anhydride.

Methoxyl Determinations in Substances Containing Sulphur.

The direct method of Zeisel cannot be employed here, since mercaptans are often produced, vitiating the determinations. In cases, however, where the methoxyl group can be split off by saponification with caustic alkali the method of F. Kaufler can be used ["Monats." (1901), 22, 1105].

The mixture of steam and alcohol vapour produced by boiling the S-containing body with KOH is freed from water by passage over heated anhydrous $CuSO_4$. The alcohol is led into cooled HI, which is afterwards heated, and the methyl iodide estimated by passage through alcoholic $AgNO_3$ in the usual manner.

A small 15 c.c. fractionating flask is used for saponification. Its side tube, at right angles to the neck, connects with a U-tube containing pumice ignited after soaking in concentrated $CuSO_4$ solution. To the U-tube is attached a Winkler's absorption apparatus half filled with hydriodic acid (sp. gr. 1·68). This in turn is attached to the ordinary Zeisel apparatus, consisting of a small fractionating flask whose side tube leads to two small flasks containing alcoholic $AgNO_3$, the latter of which is connected to a water pump.

The substance (0·3 gm.) is weighed into a small tube which, together with 3-6 c.c. aqueous KOH (sp. gr. 1·27), is put into the saponification flask. The Winkler absorber is placed in a mixture of salt and ice, whilst the U-tube is heated to 80°-90° by a water bath. The saponification is effected by heating the flask in a glycerine bath slowly, till a weak boiling occurs, and this is kept up till the contents of the flask become viscous. The glycerine bath is removed and the apparatus cooled by drawing through it a slow current of air, freed from acid by KOH and dried over $CaCl_2$. A fresh quantity of alkali is used and the operation repeated. The cooling vessel is now removed from the Winkler absorber and the latter dried externally and kept at the ordinary temperature for half an hour, air coming through slowly all the time to bring over all the alcohol from the saponification

flask and the U-tube into the hydriodic acid where it forms methyl iodide. The HI is now heated up to 130° by the bath, and the air current increased to prevent spitting. When all the methyl iodide has been distilled off, the apparatus is allowed to cool, still in a slow current of air. The time taken to reach this stage is from three to four hours. The remainder of the operation is exactly the same as in the usual Zeisel estimations.

In conjunction with Zeisel's method this modification may be used to differentiate between saponifiable and unsaponifiable methoxyl groups.

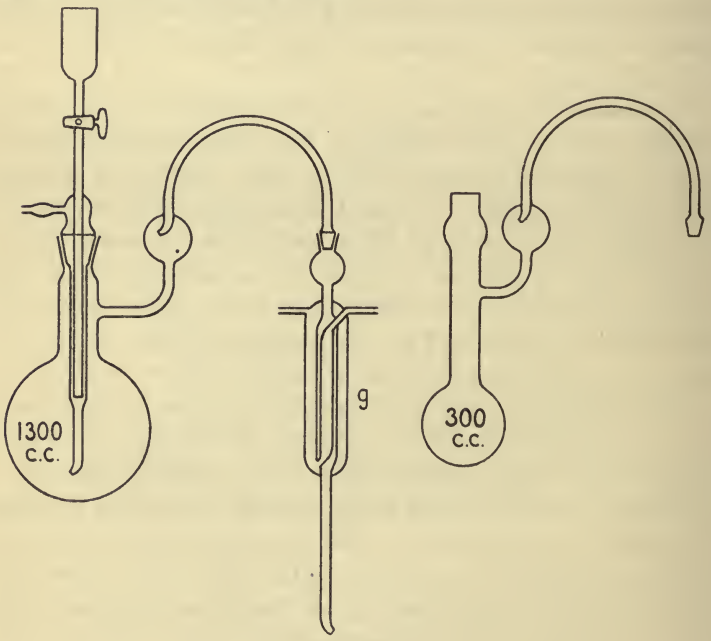
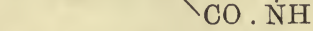


Fig. 35.

The Morgan-Cook apparatus (Fig. 35) can be used in many estimations requiring distillation. The larger flask is convenient for nitrogen determinations by Kjeldahl's method, whilst the smaller does well for acetyl or methoxyl determinations. In the latter case the tube of the condenser *g* is immediately above the alcoholic $AgNO_3$ contained in the first flask.

Methyl Attached to N Atom.

Max. Busch ("Ber." (1902), 35, 1565) has found that 1-phenyl-4-methylanilino-urazole,



the constitution of which is known from its method of synthesis, does not conform to the rule of Herzig and Meyer, but yields a portion of its methyl in the form of methyl iodide when boiled with hydriodic acid.

The production of methyl iodide in this connexion cannot therefore be taken as a conclusive proof of the presence of methoxyl. This behaviour appears to be due to the presence of the neighbouring carbonyl group, as benzoyl-phenyl-methyl hydrazine acts in a similar manner. The substances, acetyl- and benzoyl-methylaniline do not yield any methyl iodide when treated with boiling hydriodic acid.

Guido Goldschmiedt and O. Hönigschmid ["Ber." (1903), 36, 1850] have found that compounds which contain the carbonyl group attached to the carbon situated in the ortho-position to the N atom, e.g. methyl betaine of papaverinic acid, apparently give up a portion of the methyl group attached to this nitrogen as methyl iodide in the Zeisel determination ["Monats." (1903), 24, 707].

The methyl-betaines of quinolinic, pyridine 2 : 3 : 4 tricarboxylic, papaverinic and pyropapaverinic acids, derivatives of pyridine containing the grouping —CO—C—N . Me—, and also methylanthranilic acid, yield part of the methyl attached to N as methyl iodide, the more completely the greater the number of carboxyl groups present.

H. Decker ["Ber." (1903), 36, 2895] has shown that papaveraldine methiodide yields little, if any, of the N-methyl as methyl iodide.

He also describes a method based on that of Zeisel. Sarcosine, betaine, creatine, creatinine, and methylamino-acetophenone yield no methyl iodide in the Zeisel determination.

Volumetric Estimation of Methoxyl and Ethoxyl Groups.

A. Klemenc ["Monats." (1913), 34, 901].

The alkyl iodide, obtained as in the Zeisel method, is decomposed by heat, and the iodine thus produced is dissolved in KI and titrated against standard thiosulphate.

The apparatus is shown in Fig. 36. It consists of a 500 c.c. flask in which the decomposition is effected, and from which the alkyl iodide is driven by a current of CO_2-free air through a short reflux condenser into a washer, of the form shown, containing a suspension of red phosphorus in water. The lower end of this washer is closed by a cork, through which wash water can thus be drawn up or run out without disturbing the apparatus. The alkyl iodide thence passes

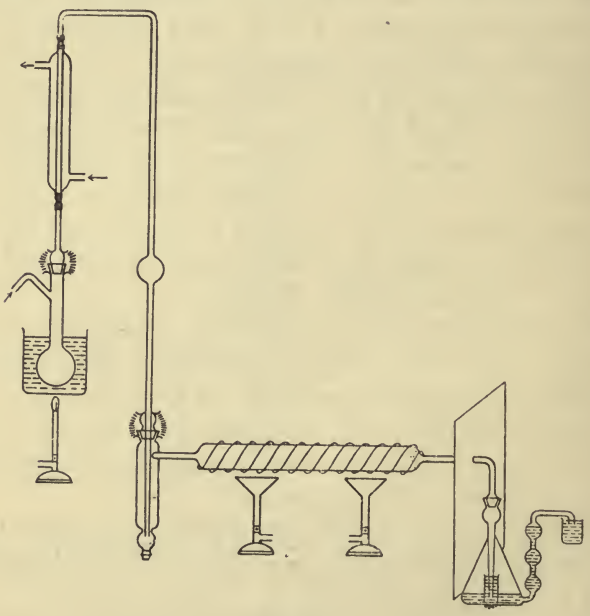


Fig. 36.

into a decomposition tube of hard glass, 25-28 cms. long and 1·2 cms. external diameter, drawn out at both ends.

The end of the tube nearest the decomposition flask is

loosely packed with 1 gm. of 25 per cent platinized asbestos. Following this is a roll of platinum foil (0·1-0·2 mm. thick and of 1·2 gms. weight), made by making a number of parallel cuts in the piece of foil and rolling it round an axis parallel to the line of incisions. A small plug of platinized asbestos separates this part of the tube from the other which is filled with fine granular ignited pumice, and it is finally closed with another plug of platinized asbestos.

The narrow end of the decomposition tube is connected by a ground joint to a tube dipping into a small cylinder (5 to 6 c.c.) contained within an Erlenmeyer flask of 60-70 c.c. capacity, communicating with the air by a Peligot tube. The inner cylinder is filled with a concentrated solution of KI, and the outer flask contains water up to the top of the entry of the Peligot tube, the open end of which dips just below the surface of water contained in the small beaker.

About 0·1 to 0·15 gm. of the substance is put into the decomposition flask, together with HI of the usual strength (sp. gr. 1·68), and heated up by means of a glycerine bath to 130°-140°. A stream of CO_2-free air is forced through the apparatus, and it is important that the alkyl iodide should enter the decomposition tube with as much air as possible. The alkyl iodide is decomposed by passage through the decomposition tube, which is kept at about 800° by the Bunsen burners below; the iodine partly sublimes in the delivery tube, and the remainder dissolves in the KI solution. When violet vapour no longer is seen in the hot end connexion of the tube the operation is completed. This should be the case in about three-quarters of an hour after the commencement. The Bunsen burners are removed from the decomposition tube and the glycerine bath, and the air current increased. The iodine in the delivery tube is washed into the flask, and the whole titrated against $\frac{N}{10}$ thiosulphate. Since a little HI is always produced in the decomposition of the alkyl iodide it must be estimated. This might be done by titration against $\frac{N}{10}$ KOH, but is most conveniently carried out by adding to the titrated iodine

solution 5 c.c. of a 4 per cent KIO_3 solution, leaving for half an hour, and titrating the freshly liberated iodine against the standard thiosulphate,

$$KIO_3 + 6HI = 3H_2O + KI + 6I.$$

A blank is done for the CO_2 present in the water used in the Erlenmeyer flask, etc., but it is impossible to allow for the CO_2 produced in the decomposition of the alkyl iodide. On account of this the results are less reliable than those got by gravimetric methods, the error being between + 0·5 and − 1·0 per cent.

Methyl iodide is completely decomposed by passage over heated pumice alone, but ethyl iodide gives olefines unless the platinum is present to complete the decomposition to CO_2 and H_2O.

THE AMINO AND IMINO GROUPS.

In the titration of organic bases, as with acids, success is based on the employment of suitable indicators. The stronger fatty amines such as methyl- and ethyl- amine can be titrated against the strong acids (HCl, etc.) using methyl orange as indicator. The aromatic amines, however, cannot be thus estimated, but good results are obtained by titrating some of these with methyl red.

Schulze ["Ber." (1887), 20, 3391] has proposed the following method for the titration of the pyridine bases.

Five c.c. of pyridine are dissolved in 100 c.c. of water, and to 25 c.c. of this solution 1 c.c. of 5 per cent aqueous $FeCl_3$ solution is added. Ferric hydroxide is precipitated according to the equation :—

$$FeCl_3 + 3C_5H_5N + 3H_2O = 3\,(C_5H_5N\,.\,HCl) + Fe\,(OH)_3$$

$N\,.\,H_2SO_4$ is now added very carefully with constant stirring until the precipitate redissolves. Each c.c. of N. acid required $\equiv 0{\cdot}07905$ gm. pyridine.

Most amines form well-defined crystalline salts with platinic and auric chlorides of the general formulæ $X_2H_2PtCl_6$ and $X_2H_2AuCl_4$ respectively where X represents one molecule of a mon-acid base. These are usually readily prepared by dissolving the base in dilute HCl and adding platinic or gold

chloride. In most cases they can be recrystallized from alcohol. Their metallic content is obtained by heating, and afterwards thoroughly igniting, a weighed quantity in a porcelain crucible, the residue being pure platinum or gold.

$$\frac{\text{Weight of Pt [Au]}}{\text{Atomic weight of Pt [Au]}} = \frac{\text{Weight of salt taken}}{\text{Molecular weight of salt}}$$

Knowing the molecular weight of the double salt, the molecular weight of the base follows from the general formulæ given above for such salts.

The molecular weight of tertiary amines can also be got from the corresponding quaternary ammonium iodides. These quaternary salts can be quickly prepared by warming with methyl iodide when they separate out and can be purified by recrystallization from alcohol.

A weighed amount of the iodide is dissolved in 200 c.c. of water in a 250 c.c. stoppered flask. $\frac{N}{10}$ $AgNO_3$ is run in with vigorous shaking until the yellow precipitate collects together, leaving the supernatant liquid colourless. When the solution no longer appears milky a little more $AgNO_3$ solution is run in and the liquid again well shaken. A few drops of ferric alum solution are now added and the excess of $AgNO_3$ titrated against $\frac{N}{10}$ potassium sulphocyanide. The weight of iodine is calculated from the amount of silver nitrate solution used.

1 c.c. $\frac{N}{10}$ $AgNO_3$ solution $\equiv$ 0·012692 gm. iodine.

The principle of the calculation is just as in the case of the metallic compounds, the general formula for the quaternary salts being $X . CH_3I$.

In all cases it must be borne in mind that the molecular weight can be got from these methods only when the acidity of the base is known and *vice versâ*.

The methods of estimation of the amino radicle vary greatly according to whether the base is aliphatic or aromatic. Those in general use for both amino and imino groups in both cases will now be given in detail.

Sudborough and Hibbert's Method.

["J. C. S." (1909), p. 477.]

The Grignard reagent reacts with primary and secondary amines according to the equations:—

$$R\,NH_2 + MeMgI = R.NHMgI + CH_4;$$
$$R_2NH + MeMgI = R_2NMgI + CH_4.$$

In the case of the primary amines if the temperature be raised to 120°-125° another molecule of CH_4 is liberated; with the secondary amines, of course, no further change occurs.

In the estimation of hydroxyl groups by this method, pure amyl ether was used as the solvent. In this research phenetole was selected as being more easily purified, but since CH_4 is somewhat soluble in this reagent a blank experiment was done to determine the extent of the solubility.

In order to purify the phenetole it is shaken with alkali, then with water, dried over $CaCl_2$ and finally distilled over sodium and kept securely stoppered.

6·09 gms. of dry magnesium turnings are added to 120 c.c. of dry phenetole, and 35·5 gms. of methyl iodide in 20 c.c. of phenetole introduced. A vigorous action ensues on warming the mixture on the sand bath, and when all the magnesium has disappeared (three-quarters of an hour), the whole is heated to the boiling-point to get rid of any excess of methyl iodide. After cooling, the clear solution is decanted off, made up to 175 c.c. with pure phenetole and kept out of contact with air.

Estimation of Secondary Amines (Imino Group).—This is carried out in just the same way as the hydroxyl determinations, page 92.

5·0 c.c. of dry phenetole with 0·1 to 0·3 gm. of substance are put into the bottle and excess (7·5 c.c.) of methyl magnesium iodide solution is placed in the small inner tube. The air is displaced by nitrogen, temperature equilibrium obtained, the solutions mixed, shaken, and the volume of methane evolved measured and reduced to N.T.P.

1 c.c. $CH_4 \equiv$ ·00067 gm. NH.

A blank experiment is made to estimate the CH_4 dissolved in the phenetole.

This method gave good results with methyl aniline, ethyl aniline, diphenylamine, etc.

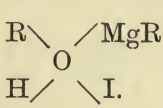
Estimation of Primary Amines (Amino Group).—The same amounts of substance and MeMgI solution are used and the volume of gas evolved at ordinary temperature measured. The mixture is then heated in an oil bath to 120° to 125° till no further evolution of gas occurs (one hour). After cooling the pressure is adjusted by the mercury columns and the volume again read and reduced to N.T.P.

$$1 \text{ c.c. } CH_4 \equiv \cdot 000357 \text{ gm. } NH_2.$$

Good results were obtained for *p*-toluidine, *β*-naphthylamine, *β*-chloraniline.

The general applicability of the estimation of hydroxyl, amino and imino groups by the Grignard reagent has been the subject of careful study by Hibbert ["J. C. S." (1912), p. 328], who came to the following conclusions:—

(1) Most hydroxy compounds give low results when phenetole is used as the solvent for the Grignard reagent. The lower fatty alcohols (up to and including propyl alcohol) behave abnormally in both phenetole and amyl ether, probably owing to the stability of some intermediate compound, such as—



(2) Aromatic and the majority of aliphatic hydroxy compounds may be accurately estimated with amyl ether, both when alone and in mixtures containing ketones, esters, etc.

(3) Aromatic amines give low values in phenetole but good values in amyl ether.

(4) The method has restricted application in the case of lower fatty amines, using either phenetole or amyl ether.

(5) Pyridine (recommended by Zerewitinoff) is perhaps the most suitable solvent for primary and secondary amines.

Estimation of Fatty Amines by Nitrous Acid.

Hans Meyer ["Analyse u. Konstitutionsermittelung organischer Verbindungen," 2nd Ed., p. 776].

Nitrous acid reacts with primary fatty amines evolving nitrogen :—

$$R.NH_2 + HNO_2 = N_2 + H_2O + R.OH.$$

The conditions for exact results from this method are very delicate. The procedure adopted by Meyer is as follows :—

The substance is dissolved in 15 c.c. of dilute H_2SO_4 or HCl in a small flask fitted with a three-holed rubber cork carrying (*a*) a very narrow inlet tube for CO_2, reaching very near the surface of the liquid; (*b*) a tap funnel drawn out at the bottom and bent up in the form of a hook. The tube of this is filled with water before the experiment; (*c*) an exit tube reaching just to the under side of the cork. This last is connected to another tube leading nearly to the bottom of a second flask containing a saturated solution of $FeSO_4$, which again is connected to Liebig's potash bulbs filled with a 3 per cent slightly alkaline solution of $KMnO_4$. From the potash bulbs a gas evolution tube leads under mercury to a gas measuring tube, filled half with aqueous KOH (sp. gr. 1·4) and half with mercury.

The CO_2 required is prepared by dropping 50 per cent H_2SO_4 (sp. gr. 1·4) on to a solution of K_2CO_3 (sp. gr. 1·45 to 1·5). A stream of such CO_2 is forced through the apparatus, and when all air has been displaced, the measuring tube is put into position, and a solution of KNO_2 (containing three times the theoretical amount of KNO_2) is allowed to flow in from the tap funnel.

The decomposition flask is heated on the water bath and at the end of the operation a little H_2SO_4, and finally a few c.c. of water are run in through the funnel. The evolved N is allowed to stand for one hour over KOH solution and twelve hours over $FeSO_4$ solution. It is then transferred to a graduated tube over water, and measured. From the volume of

N evolved the percentage of NH_2 is calculated from the equation given above.

For the application of this method to biochemistry the reader should consult the work of Van Slyke, in the "Journal of Biological Chemistry," XII. 301; XVI. 125, etc.

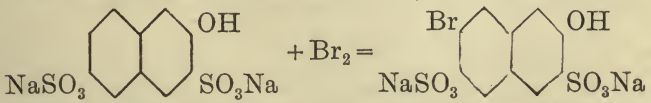
Dye Formation.

Many aromatic amines can be estimated by diazotization and coupling with a suitable hydroxy compound to give dyes which are either insoluble in water or can be salted out. The dye is filtered on a Gooch crucible, dried at 100°, and weighed. β-Naphthol in alkaline solution may be used for this purpose, but the best-known application of the method is that devised for the determination of aniline by Reverdin and De la Harpe ["Ber." (1889), 22, 1004]. The hydroxy body used for coupling is the sodium salt of R-acid (2-hydroxy 3-6 naphthol disulphonic acid).

Preparation and Standardization of R-Salt.—A known solution of R-salt is made by dissolving 20 gms. of the commercial substance in 1 litre of water. An $\frac{N}{10}$ $KBrO_3$ solution is required for the standardization and it is prepared by dissolving 0·7 gm. of the pure salt in 250 c.c. of water. The exact strength of this bromate solution must be determined by addition of KBr and excess of KI (acid) and titrating the liberated iodine by standard thiosulphate :—

$$2\ KBrO_3 + 4\ KBr + 3H_2SO_4 = 3\ K_2SO_4 + 3\ H_2O + 3\ Br_2.$$

The titration is repeated with the addition of 10 c.c. of the R-salt solution, the liquid being allowed to stand 5-10 minutes before putting in the KI. From the difference in the amounts of thiosulphate used in the two cases the purity of the R-salt may be calculated from the equation :—



An actual determination will serve to make this quite clear.

0·7131 gm. of $KBrO_3$ was dissolved in 250 c.c. of water.

Strength of thiosulphate used = $0{\cdot}982\ \frac{N}{10}$.

10 c.c. $KBrO_3$ solution required 10·5 c.c. thiosulphate.

$\therefore$ $KBrO_3$ solution was $\frac{10{\cdot}5}{10} \times 0{\cdot}982\ \frac{N}{10} = 1{\cdot}03\ \frac{N}{10}$.

20·0025 gms. of R-salt were dissolved in 1 litre.

10 c.c. $KBrO_3$ solution + 10 c.c. R-salt solution required 1·45 c.c. thiosulphate.

From the equation, 348 gms. R-salt $\equiv$ 160 gms. bromine, so that 1000 c.c. bromate solution

$$\equiv 1{\cdot}03 \times \frac{34{\cdot}8}{2} = 1{\cdot}03 \times 17{\cdot}4 \text{ gms. R-salt}$$

i.e. 1 c.c. $\equiv 1{\cdot}03 \times {\cdot}0174$ gm. R-salt.

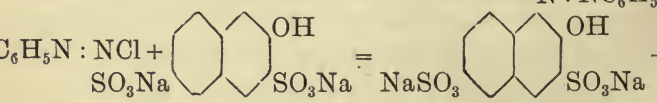
$$\text{Number of c.c. of bromate used} = 10 - 1{\cdot}45 \times \frac{10{\cdot}0}{10{\cdot}3} = 8{\cdot}6$$

Number of gms. of R-salt in 10 c.c. = $8{\cdot}6 \times 1{\cdot}03 \times {\cdot}0174$

$\therefore$ percentage purity of R-salt

$$= \frac{8{\cdot}6 \times 1{\cdot}03 \times {\cdot}0174 \times 100}{0{\cdot}200025} = 77{\cdot}05.$$

Standardization by Aniline.—About 1 gm. of pure aniline is weighed out, dissolved in 30 c.c. of HCl and made up with water to 100 c.c. The purity of the aniline may be estimated by the bromine method, p. 256. Ten c.c. of the aniline solution are diluted with water and ice, and 10 c.c. of a 20 per cent solution of $NaNO_2$ gradually added (giving excess of HNO_2). The diazotized solution is then added to 20 c.c. of the R-salt solution containing excess of Na_2CO_3. The red dye formed is thrown out of solution by a concentrated solution of NaCl :—



The dye is filtered off and the filtrate tested with (*a*) the diazonium salt, (*b*) the R-salt solution, to ascertain which of these is in excess. The amount of R-salt is varied till the filtrate from the dye is neutral to both R-salt and diazonium

salt. Thus the exact number of c.c. of R-salt solution, equivalent to the known amount of diazonium solution used, is obtained. The percentage of aniline is then calculated from the above equation. Two consecutive results with pure aniline gave 101·8 per cent and 100·3 per cent.

Acetylation of NH_2 and NH Groups.

Reverdin and De la Harpe ["Ber." (1889), 22, 1004].

1-2 gms. of the substance are weighed into a flask provided with a reflux condenser, and 5 c.c. of acetic anhydride added from a pipette having a soda-lime guard tube. In a similar flask another 5 c.c. of the anhydride are put. Both flasks are left for half an hour at the ordinary temperature, 50 c.c. of water are added to each, and both warmed on the steam bath for three-quarters of an hour to decompose the excess of anhydride. The acetic acid is titrated against standard $Ba(OH)_2$, using phenolphthalein as indicator. The difference in the two titrations gives a measure of the amount of NH_2 or NH present.

$$2RNH_2 + (CH_3CO)_2O = 2RNHCOCH_3 + H_2O$$
$$2R_2NH + (CH_3CO)_2O = 2R_2NCOCH_3 + H_2O$$

The application of the R-salt method and the acetylation method gives a ready means of analysing mixtures of aniline and methyl aniline.

In order to avoid the loss of acetic anhydride which occurs from slight volatilization owing to the heat set up in the reaction, Giraud diluted the anhydride with ten times its volume of dimethylaniline. After estimating the strength of this solution it was applied in just the same manner as the pure anhydride in the method of Reverdin and De la Harpe.

At the end of the experiment the excess was decomposed by cold water. During the longer time taken for this decomposition, however, an appreciable action takes place between the acetic anhydride and dimethylaniline with the formation of tetramethyl-diamido-diphenylmethane, thus destroying the accuracy of the results.

Vaubel's Method.

["Chem. Ztg.," 17, 465 (1893).]

The dimethylaniline is replaced by pure xylene, the composition of the acetylating mixture being 7 parts of anhydride and 100 parts of xylene.

A dry litre flask is fitted with a two-holed cork, carrying a dropping funnel and a short piece of glass tubing. The funnel has a cork carrying a piece of glass tubing reaching nearly to the bottom of the liquid and connected by a piece of rubber tubing to the other piece of tubing in the cork of the flask as in Fig. 37.

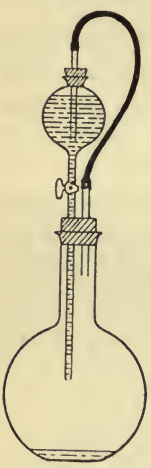


Fig. 37.

The dropping funnel should contain about 300 c.c. of water, and its delivery tube is filled with water before insertion into the cork.

1-2 gms. of the substance are acetylated in the cold by 50 c.c. of the anhydride-xylene solution. After standing for 1 hour water is run in from the dropping funnel. The displaced air has to bubble through this water, and is thus deprived of any anhydride vapour it may contain. The acetic acid from the unused anhydride is titrated with $\frac{N}{2}$ $Ba(OH)_2$, using phenolphthalein as indicator. In a similar manner 25 c.c. of the anhydride-xylene solution are decomposed by water and the acetic acid determined.

Method of A. G. Green and S. Rideal.

["Chem. News" (1884), 49, 173.]

In this paper the authors put forward a method for the estimation of nitrous acid by aniline.

Proceeding indirectly, it is possible to estimate aniline by using a standard solution of nitrite.

An $\frac{N}{10}$ solution of sodium nitrite is standardized against potassium permanganate solution.

The solution of aniline salt, containing more than twice its acid equivalent (sulphuric and hydrochloric acids in equal quantities), should be roughly decinormal.

Several experiments are now made, using the same quantity of aniline solution in each case, but varying the amount of nitrite solution within the limits of a rough determination. After standing some time, an equal volume of starch solution and potassium iodide is added to each mixture; the one in which there is a faint blue colour will show that a slight excess of nitrous acid has been added. If the solution of aniline be diluted to four times its volume with water, and the nitrite solution be run in slowly, ice is unnecessary.

For accurate results the solutions should stand in an atmosphere of carbon-dioxide or coal gas.

The preparation and standardization of the sodium nitrite solution is best done according to the directions of Kinnicut and Nef ["J. Amer. Chem. Soc." (1884), 5, 388].

A solution of 1 part by weight of $NaNO_2$ in 300 c.c. of water is prepared, and $\frac{N}{10}$ $KMnO_4$ run into 25 c.c. till the liquid is permanently pink. A few drops of dilute H_2SO_4 are now added together with a known excess of $KMnO_4$. The mixture is strongly acidified with H_2SO_4, heated to boiling, and the excess found by titration against $\frac{N}{10}$ oxalic acid. The oxidation is represented by the equation :—

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

THE NITRO GROUP.

Knecht and Hibbert's Method.

Titanous chloride quantitatively reduces nitro bodies to amines, six equivalents of $TiCl_3$ being equivalent to one NO_2 group.

Preparation and Storage of the $TiCl_3$ Solution.—Fifty c.c. of the commercial 20 per cent $TiCl_3$ solution is boiled with 100 c.c. of concentrated HCl and made up to 2¼ litres. This solution is kept in the storage bottle A (Fig. 38), which it must quite fill when freshly prepared. A is connected to both top and bottom of the burette by glass tubing, but in the latter case a bead valve is inserted at D^1. The other tube from the top of A goes to the hydrogen generator C, which consists of two parts, (*a*) an inner tube containing granulated zinc: this is drawn out to a fine point at its lower end; (*b*) an outer vessel containing HCl.

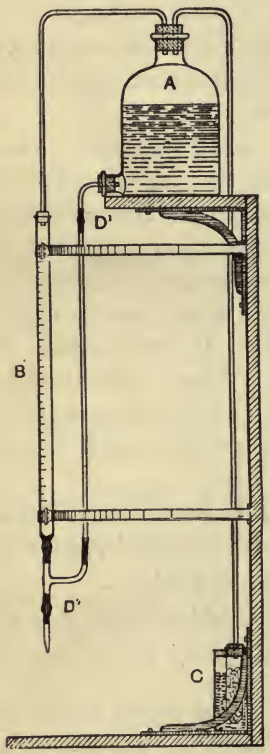


Fig. 38.—(From Knecht and Hibbert's "New Reduction Methods in Volumetric Analysis".)

The apparatus is completely filled with hydrogen by opening D^1 and filling the burette right to the top with liquid. D^2 is then opened and the liquid run out and consequently hydrogen drawn in. For correct work it is absolutely necessary to keep the $TiCl_3$ solution out of contact with air.

Standardization of $TiCl_3$.—3·5 gms. of pure ferrous ammonium sulphate are dissolved in air-free water, 100 c.c. of 5N . H_2SO_4 added, and the whole made up to 250 c.c. A

known volume (25 c.c.) is just completely oxidized by $\frac{N}{50}$ $KMnO_4$ solution and a large excess of potassium thiocyanate added. The $TiCl_3$ solution is then run in from the burette till the red colour just vanishes.

1 c.c. $TiCl_3$ solution $\equiv x$ gms. Fe″.

A standard solution of iron alum may be used for direct titration, instead of oxidizing the ferrous salt with $KMnO_4$.

Estimation of the Nitro Group.—A known weight of the nitro body is dissolved in water in a flask through which a stream of CO_2 passes. A considerable excess of the $TiCl_3$ solution is run in and the whole boiled for ten minutes to get complete reduction. The excess of $TiCl_3$ is estimated by standard ferric salt (iron alum).

Nitro bodies insoluble in water must be first sulphonated by heating on the water bath for two hours with fuming H_2SO_4.

Substances which are not easily sulphonated, e.g. dinitrobenzene, are dissolved in alcohol, and the solution allowed to pass into a known volume of $TiCl_3$ solution acidified with HCl in a conical flask, through which CO_2 is kept passing. The mixture is boiled and the excess of $TiCl_3$ estimated in the usual way.

Nitroso Bodies.—These are estimated in the same manner, four equivalents of $TiCl_3 \equiv$ one NO group.

$$NO + 4\ TiCl_3 + 4\ HCl = 4\ TiCl_4 + H_2O + NH_2.$$

For further uses of $TiCl_3$ as a quantitative-reducing agent see p. 167, and "New Reduction Methods in Volumetric Analysis," by Knecht and Hibbert (Longmans).

Limpricht's Method.

["Ber.," 11, 35 (1878).]

The majority of simple nitro bodies are quantitatively reduced by stannous chloride in the presence of HCl to amino bodies.

$$R.NO_2 + 3\ SnCl_2 + 6\ HCl = R.NH_2 + 3\ SnCl_4 + 2H_2O.$$

By using a known amount of $SnCl_2$ in excess of that required for reduction, and afterwards estimating the excess, the amount of NO_2 can be deduced from the above equation.

The following solutions are required:—

$SnCl_2$ solution: Dissolve 150 gms. of tin in concentrated HCl; decant off the liquid, to it add 50 c.c. of concentrated HCl and dilute with water to 1 litre; estimate the strength in terms of $\frac{N}{10}$ iodine.

NaOH solution: 90 gms. of NaOH and 120 gms. of Rochelle salt are dissolved in 1 litre of water.

Iodine solution in KI: $\frac{N}{10}$.

Starch solution.

0·2 gm. of the nitro compound and 10 c.c. of $SnCl_2$ solution are put into a 100 c.c. flask and warmed for at least half an hour on a water bath. The contents are made up to 100 c.c.; 10 c.c. of this are diluted with water, and soda solution added till the precipitate first formed redissolves. More water is added together with a little starch solution and the whole titrated against $\frac{N}{10}$ iodine.

1 c.c. $\frac{N}{10}$ iodine $\equiv$ ·0095 gm. $SnCl_2 \equiv$ ·000766 gm. NO_2.

Volatile liquids are weighed out in the usual thin bulb and introduced into a tube which is afterwards drawn off and sealed. This tube contains 10 c.c. of $SnCl_2$ solution, and since it has to stand but very little pressure it can be made of fairly thin glass. When closed it is well shaken

to break the small bulb inside and mix the contents, and then it is heated in a water bath and shaken from time to time. About two hours usually suffices for reduction, after which time the tube is cooled, opened, and its contents transferred to a 100 c.c. flask, made up to the mark with water, and the excess of $SnCl_2$ estimated as above.

This and all the other methods described for the estimation of nitro groups fail if other easily reducible groups are present.

Green and Wahl's Method.

["Ber.," 31, 1080 (1898).]

This method is suitable for nitro bodies which are quantitatively reduced to hydroxylamines by zinc dust in the presence of NH_4Cl.

$$R.NO_2 + 2H_2 = R.NHOH + H_2O.$$

An excess of zinc dust of known content is used for the reduction, the excess of zinc being determined by the same method as used for the original valuation.

Valuation of Zinc Dust.—A. R. Wahl ["J. Soc. Chem. Ind." (1897), p. 15].

Zinc dust suspended in water is readily dissolved by ferric sulphate according to the equation

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4.$$

The ferrous sulphate is estimated by acid $KMnO_4$ and thus the amount of zinc present is readily obtained.

For the preparation of pure ferric sulphate 500 gms. of pure $FeSO_4$ are dissolved in as little water as possible, 100 gms. of H_2SO_4 added and then, slowly, 210 gms. of 60 per cent HNO_3. A violent evolution of nitrous fumes occurs and the solution darkens but clears when all the acid has been added. The liquid is evaporated to dryness, powdered in a mortar with alcohol and filtered, the residue is washed free from acid with alcohol and finally thoroughly dried at 100° and kept well stoppered.

For the valuation of the zinc dust 0·5 gm. is put into a

500 c.c. measuring flask with 25 c.c. of cold water, well shaken up and 7 gms. $Fe_2(SO_4)_3$ added. When all the zinc (except for slight impurities) has dissolved, 25 c.c. of concentrated H_2SO_4 are added and the whole made up to the mark. Suitable portions are titrated with standard $KMnO_4$.

Estimation of Nitro Body.—Two gms. of NH_4Cl in a little water, together with 4 gms. of Zn dust and 3 to 4 gms. of the nitro-compound are put into a small flask, fitted with a rubber stopper provided with a Bunsen valve. The reduction proceeds partly in the cold and is completed by boiling for 10 to 15 minutes. The contents of the flask are allowed to settle and the liquid decanted off, the residue being washed with hot water by continued decantation. 10 gms. of $Fe_2(SO_4)_3$, dissolved in water, are added to the residue. When solution is complete the liquid is acidified with H_2SO_4, made up to 500 c.c., and titrated with $\frac{N}{10}$ $KMnO_4$. From the amount of zinc used for reduction the amount of nitro group present is calculated.

THE CARBONYL GROUP.

Ripper's Method for the Estimation of Aldehydes.

This depends on the fact that the bisulphite compounds of aldehydes are not oxidized by iodine solution, whereas free alkali bisulphite is thus oxidized.

A 0·5 per cent aqueous solution of the aldehyde is made, and 25 c.c. of this are placed in a small flask with 50 c.c. of a solution of $KHSO_3$, containing 12 gms. in 1 litre. The flask is corked and allowed to stand whilst the iodine value of 50 c.c. of alkali bisulphite is determined with $\frac{N}{10}$ iodine. After about a quarter of an hour the bisulphite production is complete, and the excess of bisulphite is estimated with the same $\frac{N}{10}$ iodine:—

If A = weight of aldehyde taken.
M = molecular weight of aldehyde.
J = weight of iodine corresponding to the weight of bisulphite combined.

$$\text{Then } A = \frac{J \times \frac{M}{2}}{126{\cdot}92}$$

For	Formaldehyde . .	$A = J \times 0{\cdot}11818$
	Acetaldehyde . . .	$A = J \times 0{\cdot}17334$
	Benzaldehyde . . .	$A = J \times 0{\cdot}41758$
	Vanillin	$A = J \times 0{\cdot}59880$

If concentrated solutions are used the HI liberated has a reducing effect on H_2SO_3.

If the aldehyde is insoluble in water, solution may be effected by the addition of a little absolute alcohol, but in no case must this exceed 5 per cent, otherwise the starch reaction will fail to be satisfactory.

E. von Meyer's Method.

["J. pr." (2), **36**, 115, (1887)].

This method depends on the estimation of the excess of phenylhydrazine, after forming the hydrazone of a known weight of aldehyde or ketone with a known volume of standard phenylhydrazine solution.

The reaction occurring between phenylhydrazine and excess of iodine is represented by the equation:—

$$C_6H_5NH.NH_2 + 2I_2 = 3HI + N_2 + C_6H_5I,$$

so that 0·1 gm. phenylhydrazine $\equiv$ 37·04 c.c. $\frac{N}{10}$ iodine.

The following method of procedure is due to Rother ["Diss.," Dresden, 1907].

The method does not allow of the formation of the hydrazone by the use of phenylhydrazine hydrochloride and sodium acetate. Only phenylhydrazine or its hydrochloride must be

present in the solution, and as the former is usually used the production of the hydrazone takes a long time for completion.

A solution of phenylhydrazine in water is made by shaking up 5 gms. of the pure redistilled base with 200 c.c. of warm distilled water, allowing to stand and pouring off from the base into a 500 c.c. flask, making up to the mark with distilled water. This solution must be well stoppered and kept in the dark.

Standardization of Phenylhydrazine Solution.—Ten c.c. of the phenylhydrazine solution are placed in a small flask with 50 c.c. water and added in small portions at a time, with shaking, to 40 c.c. $\frac{N}{10}$ iodine solution (excess) diluted with water to 300 c.c. and contained in a litre flask. After about one minute the solution is titrated with $\frac{N}{10}$ thiosulphate using starch as indicator.

Estimation of Aldehyde or Ketone.—0·5 to 1·0 gm. of the aldehyde or ketone is weighed out and placed in a 250 c.c. flask, with 30 c.c. alcohol. A known volume of the phenylhydrazine solution, which must be in convenient excess over that required for the hydrazone formation, is added and the whole well shaken in the dark for two to three minutes. The flask is allowed to stand in the dark for fifteen hours, at the end of which time the hydrazone formation should be complete. The liquid is diluted and the hydrazone filtered off, the filtrate and washings being collected in a litre flask. The bulk of liquid should be about 500 c.c. A convenient excess of $\frac{N}{10}$ iodine solution is then added and back titrated against $\frac{N}{10}$ thiosulphate.

Now 108 gms. phenylhydrazine

$$\equiv \text{M gms.} \quad \begin{matrix}\text{aldehyde}\\ \text{or}\\ \text{ketone}\end{matrix} \quad [\text{M} = \text{mol. wt.}]$$

$$\equiv 40{,}000 \text{ c.c. } \frac{N}{10} \text{ iodine solution.}$$

$$\text{If } x = \text{wt}\begin{cases}\text{aldehyde}\\ \text{ketone}\end{cases}\text{ taken}$$

v = no. c.c. iodine value used in production of hydrazone,

$$\text{then percentage of }\begin{cases}\text{aldehyde}\\ \text{ketone}\end{cases} = \frac{v \times \text{M}}{400\,x}.$$

Method of Watson Smith.

["Chem. News" (1906), **93**, 83.]

The principle of the method lies in the determination of the excess of phenylhydrazine, after forming the hydrazone of a definite amount of the aldehyde or ketone with a known volume of standard phenylhydrazine.

The excess of phenylhydrazine is estimated from the volume of nitrogen evolved on oxidation with Fehling's solution :—

$$2C_6H_5 . NH . NH_2 + O_2 = 2C_6H_6 + 2N_2 + 2H_2O \quad . \; . \; . \quad (1)$$

The following reagents are required :—

Fehling's Solution.—Mix equal volumes of solutions (*a*) and (*b*).

(*a*) $CuSO_4$ solution ; 70 gms. of crystalline salt in 1 litre of water.

(*b*) Alkaline potassium tartrate ; 350 gms. of potassium tartrate and 260 gms. KOH in 1 litre of water.

Sodium Acetate.—A 10 per cent solution.

Phenylhydrazine Hydrochloride.—A 5 per cent solution.

The apparatus required is shown in Fig. 39. A current of CO_2 is generated in the Kipp and passed through the wash bottle containing water, and then right through the whole apparatus. The reaction flask of 1 litre capacity is provided with a 3-holed rubber stopper, through which comes (*a*) an entry tube for CO_2 reaching to within 2-3 in. of the liquid ; (*b*) a tap funnel containing the phenylhydrazine solution to be estimated. This dips below the liquid, and is slightly narrowed at the end and bent upwards ; (*c*) an exit tube, which is connected to a water condenser inclined upwards, thence to

a series of absorption bulbs and an absorption flask to the Schiff's nitrometer containing a strong solution of aqueous potash (1 : 1).

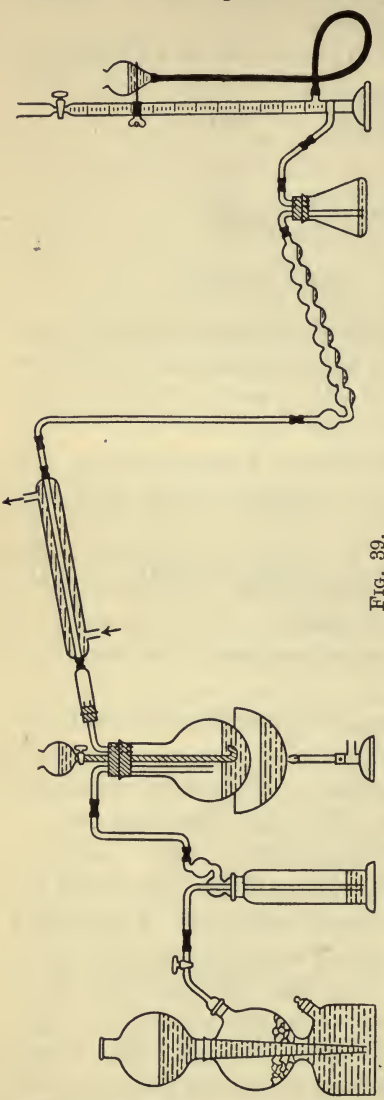


Fig. 39.

Blank Experiment. — Two hundred c.c. of Fehling's solution are introduced into the flask and covered with a thin layer of hot paraffin wax to prevent absorption of the CO_2 by the solution. The tap funnel contains just sufficient water to fill the long tube and reach above the tap.

The absorption bulbs and flask contain a mixture of equal volumes of concentrated sulphuric and nitric acids. This serves to "fix" the benzene as nitrobenzene and prevents any vapour due to the former from entering the nitrometer.

Everything being in position the flask is heated up on a water bath, and a slow current of CO_2 forced through the apparatus till all the air has been expelled, i.e. until no bubbles escape into the nitrometer unabsorbed by the KOH solution.

Ten c.c. of the phenylhydrazine solution are mixed with 15 c.c. of the sodium acetate solution, and made up with water to 100 c.c. Fifty c.c. of this are placed in the tap funnel, and slowly run into the flask. Nitrogen is evolved and swept into the nitro-

meter ; any liquid tending to distil over is condensed in the Liebig condenser and runs back again into the flask.

When the whole of the phenylhydrazine solution has been run in, the funnel is rinsed with hot water, and this liquid also run into the flask. When the bubbles of gas in the nitrometer are absorbed as fast as they appear it is disconnected and allowed to stand. The volume is read and reduced to N.T.P. either (*a*) allowing for the vapour tension of KOH solution (= approximately one-third the tension of aqueous vapour), or (*b*) transferring to a graduated tube over water.

Suppose 100 c.c. of phenylhydrazine solution $\equiv$ V c.c. N at N.T.P.

Actual Estimation.—0·1 to 0·5 gm. of the aldehyde or ketone is mixed with a measured quantity of the phenylhydrazine hydrochloride solution (10 c.c.) and one and a half times this quantity of the sodium acetate solution (15 c.c.) added, together with about 40 c.c. water, in a 100 c.c. flask, and heated for 10-15 minutes on a water bath. This is sufficient for the formation of the hydrazones of all ordinary aldehydes and ketones. Water is then added to the cooled mixture up to the mark. Fifty c.c. of this are placed in the tap funnel and the estimation made as before.

Let 100 c.c. of this solution $\equiv v$ c.c. N at N.T.P. If x = weight of aldehyde or ketone taken then x gms. aldehyde or ketone $\equiv$ V $- v$ c.c. N.

$$\mathrm{R.CHO + H_2N.NH.C_6H_5 =}$$
$$\mathrm{RCH:N.NH.C_6H_5 + H_2O} \quad \ldots \quad (2)$$

From equations (1) and (2) :—

M gms. of aldehyde or ketone $\equiv$ 22400 c.c. N. [M = mol. wt.]
x ,, ,, ,, ,, ,, $\equiv$ (V $- v$) c.c. N.

$$x = \frac{\mathrm{M(V} - v)}{22400}$$

N.B.—Care must be taken to select a suitable weight of the aldehyde or ketone. A volume of 20-25 c.c. of N in each case should be aimed at when possible.

A modification of this method has been proposed by J. S. MacLean ["Biochem. J." (1913), **7**, 611].

Instead of measuring the nitrogen evolved, the cuprous oxide precipitated is estimated volumetrically by the method employed by Bertrand for glucose (p. 156). It was found that the amount of Cu_2O precipitated from the Fehling's solution by a definite weight of phenylhydrazine was constant, and the results obtained for the substance under investigation (pyruvic acid) were such as to justify its proposition as a general method for the determination of the carbonyl group. In view of its possibilities in this direction the standardization of the phenylhydrazine and the procedure in the case of pyruvic acid will now be described.

Standardization of Phenylhydrazine.—Five c.c. of a solution of phenylhydrazine freshly prepared from re-distilled material, containing 3·5 gms. in 100 c.c. of 50 per cent acetic acid, are diluted with water to 100 c.c. and allowed to stand at the ordinary temperature for half an hour.

The two solutions A and B constituting the Fehling's solution are made up as for Bertrand's glucose estimation, viz. :—

A. 40 gms. crystalline $CuSO_4$ per litre.
B. 200 gms. Rochelle salt, 150 gms. NaOH } " "

Twenty c.c. of A and B are mixed and added to 10 c.c. of the diluted phenylhydrazine solution and left to stand for half an hour, after which time the reduction is complete. The Cu_2O is filtered on a Gooch crucible under low pressure, and after washing is dissolved in ferric sulphate, and the $FeSO_4$ produced is titrated with $\frac{N}{10}$ $KMnO_4$.

Thus one finds that

$$1 \text{ c.c. } \frac{N}{10} KMnO_4 \equiv x \text{ gms. phenylhydrazine.}$$

Estimation of Pyruvic Acid.—1-5 gms. of the acid were dissolved in 100 c.c. of water.

From 2-10 c.c. were diluted to 80 c.c. and 5 c.c. of a

solution of phenylhydrazine of approximately 4 per cent strength were added, and the mixture made up to 100 c.c. and left for half an hour.

Five c.c. of the hydrazone solution were diluted to 100 c.c., and also left to stand for half an hour. The hydrazone separating out was filtered off, 10 c.c. of the filtrate added to 40 c.c. of Fehling's solution, and the Cu_2O estimated as above. Ten c.c. of the control solution of phenylhydrazine were similarly treated.

Strache's Method.

["Monats." (1891), 12, 514; (1892), 13, 299.]

This method is the original from which Watson Smith developed his modification. The apparatus is simple but requires great skill in manipulation in order to obtain good results.

The chief differences between Strache's original method and Watson Smith's modification are as follows:—

1. The air is driven out from the apparatus by a current of steam which also serves for sweeping out the nitrogen. This avoids the use of CO_2 and paraffin wax over the Fehling's solution.

2. The benzene is not "fixed" in any way, so that in the measurement of the volume of nitrogen, the vapour pressure of benzene has to be allowed for.

3. The gas is collected in an ordinary measuring tube over water.

By this method, therefore, the apparatus is greatly simplified as is shown in Fig. 40.

Water is boiled in the first flask and the steam passes under the Fehling's solution in the second flask which is kept boiling. The delivery tube from the latter, made in two parts joined by rubber tubing, runs into the water trough, in which is also a measuring tube filled with water.

The proportions and reagents used and the method employed are exactly as in the method of Watson Smith; 50 c.c. of the mixture being introduced into the tap funnel as before.

The water in the first flask is boiled up and likewise the 200 c.c. of Fehling's solution in the second flask, till a good

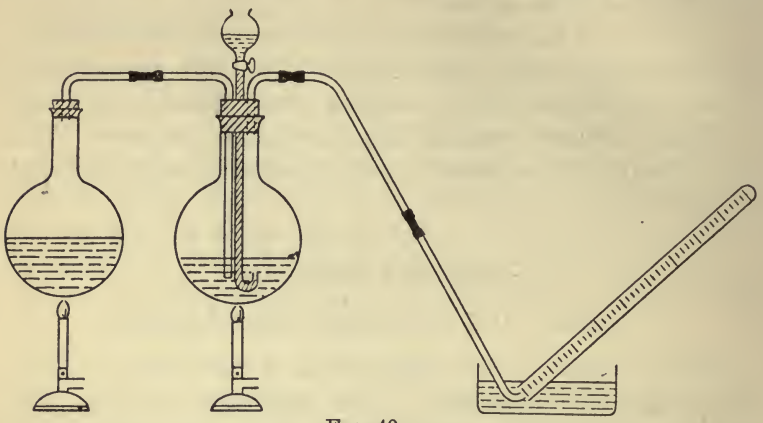


Fig. 40.

stream of vapour comes from the upper part of the delivery tube. The lower part of this is then fastened on and the water vapour finally drives out all the air so that no uncondensed bubbles appear in the graduated cylinder placed for gas reception.

The phenylhydrazine solution is then run in from the tap funnel and the N evolved is collected as before. The tube with its contained N is brought into a trough of cold water and allowed to come to air temperature. Its volume at N.T.P. is calculated, allowing for the combined tension of benzene and water vapour.

Temperature in C°.	Combined tension of aqueous vapour and benzene vapour in mms. Hg.
15	72·7
16	76·8
17	80·9
18	85·2
19	89·3
20	93·7
21	98·8
22	103·9
23	109·1
24	114·3
25	119·7

Two or three of these estimations can be run, one directly after the other, using the same Fehling's solution.

To ensure saturation of N by benzene vapour, a little benzene may be passed into the measuring tube containing the nitrogen. The above correction table then fully holds.

It is difficult to get all the air displaced from the apparatus by steam, so that the results are often too high.

Petrenko-Kritschenko's Method.

["Ber." (1901), 34 (2) 1702.]

This is the only method based on oxime formation. The oximes in dilute aqueous solution do not combine with acids, whereas free hydroxylamine does. The oxime is formed in alcoholic solution by the action of a definite amount (in excess) of freshly made hydroxylamine sulphate with its exact equivalent of $BaCl_2$. All estimations were made by mixing together the solutions so that the combined solution was 50 per cent alcoholic and of $\frac{N}{100}$ concentration. The excess of hydroxylamine was titrated with standard HCl using methyl orange as indicator.

This method has been criticized by Stewart ["J. C. S.," 87, 410 (1905)], who used a method of Meyeringh. See "Estimation of Hydroxylamine," p. 266.

Accounts of the velocity of formation of oximes, phenylhydrazones and bisulphite products of various ketones are given by Petrenko-Kritschenko ["Ber.," 34, 1702 (1901)]; ["Ann.," 15, 150 (1905)]; A. W. Stewart ["J. C. S.," 87, 410 (1905)].

A most important investigation of the quantitative methods of determining aldehydes has been recently made by Feinberg ["Amer. Chem. J." (1913), 49, 87-116]. A summary of this work is therefore given at this point.

The methods employed were (1) the bisulphite method, (2) the neutral sulphite method, (3) hydrazone precipitation. The aldehydes used were formaldehyde, benzaldehyde, salicylaldehyde, *p*-hydroxy benzaldehyde, anisic aldehyde, and vanillin.

(1) The Bisulphite Method.

The method of procedure was essentially that of Ripper (p. 118). A 1 per cent aldehyde solution was placed in a stoppered Erlenmeyer flask with 10-25 c.c. of a 3 per cent solution of sodium bisulphite. After fifteen minutes the solution was titrated with $\frac{N}{10}$ iodine solution till the blue colour with starch persisted for an instant. A blank was made under the same conditions, and the difference in the titrations gave the iodine value of the amount of aldehyde used.

	Formaldehyde.	Benzaldehyde.	Salicylaldehyde.	*p*-hydroxy benzaldehyde.	Anisic aldehyde.	Vanillin.	
1 gm. iodine ≡	0·1186	0·4118	0·4808	0·4808	0·5360	0·5990	gm.

The percentage of the theoretical obtained by this method for the various aldehydes were :—

Formaldehyde.	Benzaldehyde.	Salicylaldehyde.	*p*-hydroxy benzaldehyde.	Anisic aldehyde.	Vanillin.
98·67	93·90	81·70	87·39	90·16	95·5

The discrepancies are due to the hydrolysis in solution of the bisulphite compounds, which varies in extent according to the nature of the aldehyde. Of those used, that of formaldehyde is the least, and that of salicylaldehyde the most hydrolyzed.

By varying the conditions he came to the conclusion that in all cases the best results are got when the amount of bisulphite in excess is that which requires about 50 c.c. $\frac{N}{10}$ iodine for titration in a volume of about 50 c.c. The most convenient strength of bisulphite is 2-3 per cent, and 25 c.c. of such a solution can be handled without any great error. Potassium bisulphite is of the same efficiency as sodium bisulphite.

(2) The Neutral Sulphite Method.

Seyewetz and co-workers have applied this method to formaldehyde and acetaldehyde (p. 245). By working with dilute solutions the end point was found to be indistinct so that a strong solution of the aldehyde and $\frac{N}{2}$ acid were employed. The conditions were as follows:—

(*a*) *Formaldehyde.*—2-5 gms. of a 34 per cent solution were weighed into a stoppered Erlenmeyer flask and neutralized with $\frac{N}{2}$ NaOH and two drops of phenolphthalein; 50 c.c. of neutral sodium sulphite solution were added for every 2 gms. of aldehyde. The mixture was allowed to stand for half an hour and then titrated with $\frac{N}{2}$ H_2SO_4 to absence of pink colour. The amount of acid required by a blank, containing an amount of sulphite equal to that left uncombined in the determination, is subtracted from the amount required in the determination (as recommended by Russ and Larsen).

$$R.CHO + Na_2SO_3 + H_2O = RC(OH)\,NaHSO_3 + NaOH.$$

(*b*) *Benzaldehyde.*—About 1 gm. was put into a well-stoppered flask with 10 c.c. alcohol and washed down with 10 c.c. water. The aldehyde was neutralized with $\frac{N}{10}$ alkali using six drops of a 1 per cent solution of phenolphthalein as indicator; 50 c.c. of neutral sodium sulphite solution were added and titrated with $\frac{N}{2}$ H_2SO_4 till the pink colour disappeared. A blank containing 35 c.c. sulphite solution (the amount calculated to be left unabsorbed) was carried out alongside the determination. The alkali required to neutralize the aldehyde was calculated to benzoic acid, and this weight of acid subtracted from the weight of the sample before calculating the percentage of aldehyde.

Applying these conditions to the other aldehydes, it was found that anisic aldehyde alone could be estimated with any

degree of accuracy. During neutralization, or after the addition of sulphite, coloured compounds were formed, rendering it impossible to titrate the solutions.

The percentage of the theoretical given by this method were :—

Formaldehyde.	Benzaldehyde.	Salicylaldehyde.	*p*-hydroxy benzaldehyde.	Anisic aldehyde.	Vanillin.
98·40	98·52	—	—	93·62	—

(3) Hydrazone Precipitation.

With p-bromphenylhydrazine.—It was sought to see whether the method of Hanus for vanillin (p. 249) was generally applicable. The solutions were about 1 per cent, and whenever possible were in aqueous solution, or only as small a quantity of alcohol or acetic acid used as was required to keep the aldehyde in solution, when the desired concentration was got by dilution with water.

The hydrazones of benzaldehyde and salicylaldehyde formed badly, were non-crystalline and gave turbid filtrates, so that the results were low (93 per cent). It was found to be impossible to estimate formaldehyde by this method. The other three aldehydes gave good results, the procedure being as follows :—

(*a*) *p-hydroxy benzaldehyde.*—25 c.c. of a 1 per cent solution of the aldehyde in water containing 40 c.c. of alcohol in 500 c.c. were treated with 75 c.c. hot water containing 2 to 3 times the calculated amount of *p*-bromphenylhydrazine. The precipitation was conducted at 50°. The remainder of the process was as for vanillin q.v.

Weight of hydrazone × 0·4193 = weight of *p*-hydroxybenzaldehyde.

(*b*) *Anisic Aldehyde.*—A 1 per cent solution of the aldehyde in acetic acid (90 c.c. glacial in 500 c.c. water) was used. The precipitation was conducted as for vanillin, but the precipitate only stood one hour instead of five, before filtering.

Weight of hydrazone × 0·4460 = weight of anisic aldehyde.

(*c*) *Vanillin.*—See page 249.

The results obtained in percentage of the theoretical were—

Formaldehyde.	Benzaldehyde.	Salicylaldehyde.	*p*-hydroxy benzaldehyde.	Anisic aldehyde.	Vanillin.
—	92·61	93·54	99·93	99·23	99·03

With p-nitrophenylhydrazine.—Acetone, acetaldehyde and benzaldehyde, are stated to be quantitatively precipitated by *p*-nitrophenylhydrazine, so that this reagent was tested as to its general applicability. The aldehyde solutions were as in the previous method, and the precipitant was freshly prepared when required by filtering a solution in either 30 per cent $H\bar{A}$ or cold dilute HCl.

The acetic acid method is the most accurate known for benzaldehyde.

A 1 per cent solution of benzaldehyde in 12 per cent acetic acid was prepared, and 25 c.c. of this were diluted with 50 c.c. of water and 30 c.c. of 30 per cent $H\bar{A}$, containing about twice the calculated quantity of *p*-nitrophenylhydrazine then added. The precipitate was allowed to stand five hours, filtered on a Gooch, washed with 10 per cent $H\bar{A}$ to absence of strong colour with dilute alkali, and dried at 105°-110°.

Weight of hydrazone × 0·4400 = weight of benzaldehyde. If the amount of benzoic acid associated with the aldehyde is separately estimated and subtracted from the weight of aldehyde used, the method gives results 99 per cent theoretical.

Salicylaldehyde under the same conditions gave 95·5 per cent theoretical; anisic aldehyde, 100 per cent; *p*-hydroxy benzaldehyde, 101·5 per cent; vanillin, 102 per cent. For general application dilute HCl is recommended, and the estimations were carried out as follows:—

The *p*-nitrophenylhydrazine dissolved in dilute HCl (approximately normal strength) was added, drop by drop, from a pipette into the aldehyde solution, which had previously been diluted with 75 c.c. of water. The mixture was stirred vigorously during precipitation and allowed to stand half an hour before filtration. It was washed on a Gooch with dilute HCl, and then with water to absence of HCl, dried at 105°-110° and weighed.

Hydrazone × 0·4400 = Benzaldehyde.
× 0·4747 = Salicylaldehyde.
× 0·4747 = *p*-Hydroxy benzaldehyde.
× 0·5019 = Anisic aldehyde.
× 0·5353 = Vanillin.

The results in percentage of the theoretical under these conditions were :—

Formaldehyde.	Benzaldehyde.	Salicylaldehyde.	*p*-hydroxy benzaldehyde.	Anisic aldehyde.	Vanillin.
75·81	98·70	95·33	99·72	100·58	99·90

This investigation has therefore shown that for formaldehyde the volumetric methods are best, whereas for salicylaldehyde, *p*-hydroxy benzaldehyde, anisic aldehyde, and vanillin the precipitation methods give the best results. Good results for benzaldehyde are got by both volumetric and gravimetric processes.

CHAPTER IV.

ESTIMATION OF SOME COMPOUNDS OF TECHNICAL IMPORTANCE.

CARBOHYDRATES.

The Polarimeter.

Polarization by Double Refraction.—When a beam of light impinges on a rhombohedron of calc spar, it is split up into two rays. Indeed, this phenomenon is general with all crystals except those belonging to the cubic series, but in all cases the incident beam must not coincide with the optical axis of the crystal.

Both these rays are polarized, that is to say, the vibrations of light proceed in a single plane instead of, as with ordinary light, in an infinite number of planes; the two emergent rays are, however, polarized in planes perpendicular to one another. To utilize this property in the construction of physical instruments, it is necessary to separate the two beams. This is accomplished by means of a Nicol's prism, which consists of two specially constructed wedge-shaped crystals of Iceland spar cemented together by means of Canada balsam; the sides are then blackened and inserted in a tube. The ordinary ray, which is most refracted, is reflected away by the film of balsam, but the extraordinary ray which vibrates in the plane of the principal section passes through the prism and emerges at the other end. Two such prisms are used in every polarimeter, one being the analyser and the other the polarizer. The latter is stationary, but when the analyser is revolved, different amounts of light pass through the combination according to the angle through which the

analyser has been turned. The polarized ray from the polarizer will follow its natural course as long as it is able to vibrate in the same axial plane.

When the axial planes of the two prisms are perpendicular to one another, the Nicols are said to be crossed and no light passes through the system. Should the prisms be placed so that their axial planes are parallel, all the light will then pass, and in positions between these extremes a partial extinction occurs.

Many liquids and solutions of solids possess the property of being able to rotate the plane of vibration of polarized light; they are said to be optically active. By reason of this, many types of polarimeters have been devised in order to estimate the amount of active substance present in a known volume of solution. The best known of these are Laurent's ["Dingl. Poly. J.," 1877, 223, 608] and Lippich's ["Z. Instrument," 2, 167, 14, 326] half-shadow polarimeters, which differ in the method of producing the half-shadow.

The Laurent Polarimeter.—The polarizer is fixed but the analyser can be rotated by means of a lever or screw either to the left or to the right. Behind the polarizer is placed a thin plate of quartz, cut plane and parallel to its optical axis, of thickness depending on the wave length of the light employed, and mounted on glass so that it covers one-half of the field of vision. The rays emerging from the quartz plate are transformed by the analyser, at the end point, into light of the same intensity and amplitude as in the other half of the field. The half-shadow effect is produced by reason of the symmetrical inclination of the two planes of vibration to the optical axis of the plate.

The Laurent apparatus must be used with monochromatic light such as is obtained from a sodium flame.

Lippich's instrument can be used for all kinds of light. Instead of a quartz plate, there is a small Nicol prism which covers half the field of vision.

A polarimeter is shown in Fig. 41.

A.—Analyser which can be rotated independently of the graduated circle.

F.—Telescope with eyepiece.

P.—Polarizing prism. It may be rotated to alter the angle of half-shadow by *h*.

S.—Lens and crystal of potassium bichromate.

K.—Graduated disc. This is provided with verniers *n* and *n'* past which the disc can be rotated with the analyser and telescope, by means of the arrangement at T.

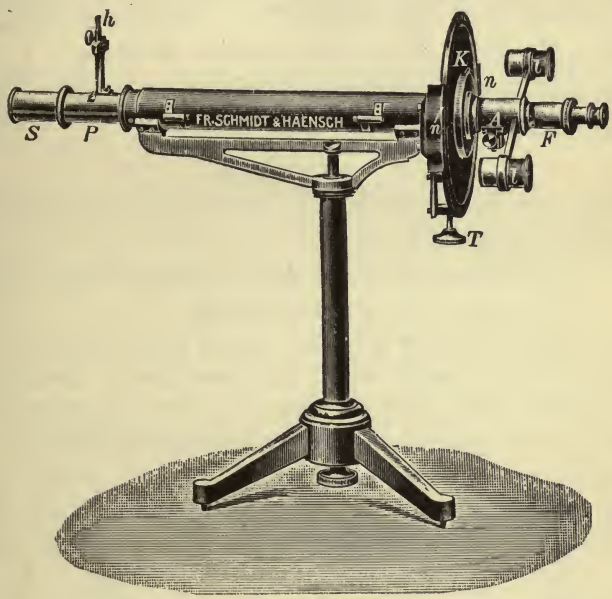


FIG. 41.

The observation tube is placed in the middle tube of the apparatus protected from daylight by means of a cover.

To determine the direction of rotation, which may be more than 180° in one direction, it is the general rule to take that in which the analyzer is rotated to give the end point through less than 90°.

The angle of rotation depends on :—

(i) The substance under examination.

(ii) Length of observation tube.

(iii) Wave length of light used.

(iv) Temperature of the experiment.

The specific rotation of an active liquid is

$$\left[a\right]_D = \frac{a}{l \cdot d}$$

where a = observed angle of rotation.
l = length of the tube in decimetres.
d = density of the liquid.

Taking into consideration the temperature and the wave length of the light, the specific rotation becomes $\left[a\right]_D^{20°}$ at a temperature of 20° C. using the D line (sodium light).

For a solid in solution,

$$\left[a\right]^{20°} = \frac{100\,a}{l \cdot c}$$

where a = observed angle
c = number of gms. of solid in 100 c.c. of solution.
l = length of tube in decimetres.

Use of the Polarimeter.—A sodium light is placed 6 in. away from the polarizer and of the instrument. An observation tube filled with distilled water is placed in position and the eyepiece is focussed on the line dividing the field of view. The zero point is determined, where the two halves of the field are equally illuminated, by rotating the analyser, using both the verniers provided to correct eccentricity, keeping h fixed.

A sugar solution (10 per cent) is brought to a uniform temperature in a thermostat and some is quickly transferred to a clean observation tube. Care is taken that the liquid fills the tube and that no bubbles are left. This can be ensured by taking out the glass window of the cap, and sliding it over the top of the filled tube held vertically. On screwing the cap into position, the tube is ready for use.

The angle of rotation is observed, several readings being taken.

In exact work, it is necessary that the observation tube should be jacketed with a liquid at a known temperature.

An observation tube and a tube surrounded by a jacket are shown in Figs. 42 and 43.

Polarimeters may be used for the examination of optically active liquids other than sugar solutions. In technical practice it is usual to employ for the latter special instruments termed saccharimeters. In these the scale expressing angular rotation is replaced by one graduated according to a system indicating percentages.

This is rendered possible by the use of a quartz wedge compensation (Soleil). The polarizer and analyser are

Fig. 42.

stationary, the rotation of the solution being read by moving a wedge of quartz between the solution and analyser until the rotation of the wedge at a certain thickness, neutralizes or compensates the rotation of the sugar solution. A scale reading in percentages is attached to the wedge. Small disturbances due to the slight differences in rotation dispersion between the quartz and the solution are nullified by a filter of potassium bichromate. The 100° point of the scale

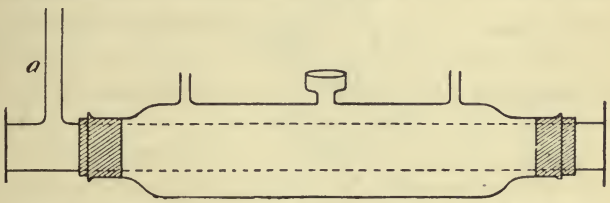


Fig. 43.—(From Findlay's "Practical Physical Chemistry").

is based upon the rotation of a definite or normal weight of pure chemical sucrose dissolved in water to 100 c.c., measured in a two-decimetre tube at a certain temperature.

Ventzke Scale.—["J. prak. Chem.," 25, 84, 28, 111.] The rotation value of the 100° point of the modern Ventzke scale is equal to 34·657 circular degrees for pure sodium light. Schrönrock ["Z. Ver. deut. Zuckerind," 54, 521].

The modern specification of the Ventzke scale as advocated by the International Sugar Commission held in Paris, 1900, is given later.

For details of saccharimeters see "Methods of Sugar Analysis" C. A. Browne.

Determination of Sugars from Angular Rotation.—

$$c = \frac{100\ a}{l \times [a]_D} \text{ or } p = \frac{100\ a}{l \times d \times [a]_D}.$$

The concentration formula is used where a definite weight of substance is made up to a known volume before polarization.

In case a sugar solution of known density is polarized directly, then the percentage formula is employed.

Formulæ for calculating the concentration in grams per 100 c.c. of different sugars from the angular rotation a in a 2-dm. tube ["Sugar Analysis," C. A. Browne]:—

1. Arabinose $c = \frac{100\ a}{2 \times (+\ 104{\cdot}5)} = 0{\cdot}4785\ a$
2. Xylose $c = \frac{100\ a}{2 \times [+\ 19{\cdot}0]} = 2{\cdot}6316\ a$
3. Glucose $c = \frac{100\ a}{2 \times (+\ 52{\cdot}8)} = 0{\cdot}9470\ a$
4. Fructose $c = \frac{100\ a}{2 \times (-\ 92{\cdot}5)} = 0{\cdot}5405\ a$ (left degrees)
5. Galactose $c = \frac{100\ a}{2 \times (+\ 81{\cdot}0)} = 0{\cdot}6173\ a$
6. Sucrose $c = \frac{100\ a}{2 \times (+\ 66{\cdot}5)} = 0{\cdot}7519\ a$
7. Maltose $c = \frac{100\ a}{2 \times (+\ 138{\cdot}0)} = 0{\cdot}3623\ a$
8. Lactose $c = \frac{100\ a}{2 \times (+\ 52{\cdot}5)} = 0{\cdot}9524\ a$
9. Raffinose $(+\ 5H_2O)$ $c = \frac{100\ a}{2 \times (+\ 104{\cdot}5)} = 0{\cdot}4785\ a$
10. Raffinose (anhydride) $c = \frac{100\ a}{2 \times (+\ 123{\cdot}15)} = 0{\cdot}4060\ a.$

The percentage $p.$ of a sugar in solution is equal to the value of c expressed above, divided by the specific gravity of the solution.

Methods of Polarizing Raw Sugars.—The rules of the International Commission for Unifying Methods of Sugar Analysis (Paris, 1900) are as follows :—

"In general all polarizations are to be made at 20° C.

"The verification of the saccharimeter must also be made at 20° C. For instruments using the Ventzke scale 26 gms. of pure dry sucrose, weighed in air with brass weights, dissolved to 100 metric c.c. at 20° C. and polarized in a room, the temperature of which is also 20° C. must give a saccharimeter reading of exactly 100·00.

"The temperature of the sugar solution during polarization must be kept constant at 20° C.

"For countries where the mean temperature is higher than 20° C., saccharimeters may be adjusted at 30° C. or any other suitable temperature, under the conditions specified above, provided that the sugar solution be made up to volume and polarized at the same temperature.

"In effecting the polarization of substances containing sugar employ only half-shade instruments.

"During the observation keep the apparatus in a fixed position and so far removed from the source of light that the polarizing Nicol is not warmed.

"As sources of light, employ lamps which give a strong illumination such as triple gas burner with metallic cylinder, lens and reflection; gas lamps with Welsbach burner; electric lamp; petroleum duplex lamp; sodium light.

"Before and after each set of observations the chemist must satisfy himself of the correct adjustment of his saccharimeter by means of standardized quartz plates. He must also previously satisfy himself of the accuracy of his weights, polarization flasks, observation tubes and cover-glasses. (Scratched cover-glasses must not be used.) Make several readings and take the mean thereof, but no one reading may be neglected.

"In making a polarization use the whole normal weight for 100 c.c. or a multiple thereof, for any corresponding volume.

"As clarifying and decolorizing agents use either subace-

tate of lead, alumina cream, or a concentrated solution of alum. Bone black and decolorizing powders are to be excluded.

"After bringing the solution exactly to the mark at the proper temperature, and after wiping out the neck of the flask with filter paper, pour all of the well-shaken clarified sugar solution on a rapidly acting filter. Reject the first portions of the filtrate and use the rest, which must be perfectly clear for polarization."

Preparation of Reagents.—1. Sub-acetate of lead solution :—

Prepare by heating to boiling a mixture of 430 gms. of normal lead acetate and 130 gms. of litharge with a litre of water for half an hour. Cool the mixture and dilute the clear supernatant liquid with boiled-out water to 1·25 sp. gr. (A.O.A.C.). Stock solutions should be protected from atmospheric carbon dioxide by means of soda-lime tubes.

Clarification by this agent introduces several errors :—

(i) Due to the volume occupied by the precipitate.

(ii) Due to an appreciable effect on the optical activity and reducing power of any invert sugar contained in the solution. Watts and Tempany. ["J. Soc. Chem. Ind.," 1907, **27**, 53].

See also, Bates and Blake ["J. Amer. Chem. Soc.," 1907, **29**, 286]; Pellet ["Bull. Assoc. Chim. Sucr. Dist.," 1906, **23**, 1466]; Sawyer ["J. Amer. Chem. Soc.," 1904, **26**, 1631]; Sachs ["Zeit. ver. deut. Zuckerind.," 1880, **30**, 229].

2. Alumina Cream.—Prepare a cold saturated solution of alum in water and divide into two unequal portions. Add a slight excess of ammonium hydroxide to the larger portion and then add by degrees the remaining alum solution until a faintly acid reaction is secured. ["Methods of Analysis by the Association of Official Agricultural Chemists," Bull. 107, (revised), "U.S. Bur. of Chem.," page 40.]

It is very important to select a proper clarifying agent; rapid filtration and brightness of clarification in conjunction with a minimum error being considered. The smallest

quantity of clarifying agent is used in all cases. Alumina cream is used with products of the highest state of purity.

Neutral lead acetate is used for slight discolorations. Where the above are without action, lead subacetate, basic lead nitrate, or lead acetate and hypochlorite are employed.

Animal charcoal or hydrosulphites are used when all other means are unavailing.

Clarification of the Solution of Sugar.—Weigh out a standard quantity of the sample and dissolve in 50 c.c. water in a 100 c.c. flask. Should the solution be colourless, it is diluted to the 100 c.c. mark with water and immediately polarized. If the liquid is coloured, one of the reagents mentioned above should be employed to decolorize or clarify it.

Whichever method is used, the mixture is shaken violently and then allowed to stand for a few minutes to allow any precipitate to settle. The flask is now filled to the mark with water, the froth destroyed by the addition of a few drops of ether, water added exactly to the mark, and the liquid filtered through a dry filter paper. It is advisable to reject the first portion of the filtrate.

Invert or Double Polarization.—Herzfeld ["Zeit. Ver. deut. Zuckerind.," 1888, 38, 699].

The original method of sugar inversion proposed by Clerget ["Comp. rend.," 16, 1000; 22, 1138; 23, 256; 26, 240; "Ann. Chem. Phys." (3), 26, 175] has been modified by Herzfeld and is the one most generally employed.

The half-normal weight (13·00 gm.) of product is placed in a 100 c.c. flask with 75 c.c. water; after solution of soluble sugars 5 c.c. of hydrochloric acid (sp. gr. 1·188) are added, and the flask heated in a water bath to a temperature between 72° and 73° C. When the thermometer in the flask registers 69°, the solution is heated at this temperature with gentle rotation for 5 minutes. The flask, which should now have been on the bath from 7½ to 10 minutes, is cooled rapidly to 20° C., the thermometer washed, and the contents of the flask made up to 100 c.c. After filtering, the solution is polarized as above.

Modifications.—1. After cooling the solution, the free

acid is carefully neutralized with sodium hydrate (avoiding excess). While this method removes the influence of the acid, a new disturbing factor is introduced by the presence of the sodium chloride. The latter is, however, of minor importance.

2. Tolmon ["Bull., 73, U.S. Bur. of Chem.," 69] has found that 2 gms. of citric acid will invert 100 c.c. sucrose solution in 30 minutes at the temperature of boiling water.

3. (*a*) Inversion by yeast, O'Sullivan and Tompson ["J. Chem. Soc.," 1891, 59, 46].

(*b*) Inversion by invertase, Hudson ["J. Ind. Eng. Chem.," 2, 143].

Decolorization of Inverted Solutions.—1. Use of a shortened observation tube. Any errors are multiplied by the factors necessary, hence this method is somewhat unsatisfactory.

2. Use of zinc dust, sodium sulphite, etc. The destruction of colour is brought about by nascent hydrogen in the first case and by sulphur dioxide in the second. Use only small amounts of these reagents.

3. Use of animal charcoal. This reagent should not be used in direct polarization as it absorbs sucrose to a large extent. It can be used safely with invert sugar solutions, but must be previously washed with dilute hydrochloric acid, washed, and dried.

Two to five gms. of fine charcoal are placed in a filter and the sugar solution poured through in portions of about 10 c.c. Discard the first runnings of about 25-30 c.c.

Analysis of Sugars by Chemical Methods.

Preparation of Fehling's Solution.—Dissolve 34·64 gms. of copper sulphate in 500 c.c. water. A second solution is prepared containing 60 gms. caustic soda and 173 gms. Rochelle salt (sodium potassium tartrate) in 500 c.c. water. Equal volumes of the two solutions are mixed before use.

Standardization of Fehling's Solution.—Equal volumes of the two solutions are mixed and 20 c.c. of the mixture are titrated against a solution of pure glucose as follows:—

Some pure glucose is dried overnight in a vacuum desiccator and an approximately 1 per cent solution is made—the exact strength being noted.

Twenty c.c. of the Fehling's solution are then placed in a conical flask and diluted with boiled-out distilled water to a mark on the flask (about 40-60 c.c.).

A rough titration is made to determine the approximate position of the end point; then proceed as follows:—

Boil the Fehling's solution, run in glucose to within 2 c.c. of the end point. Boil for 1 minute. Add another 1·5 c.c. and again boil for 1 minute. Then run in two drops at a time, boiling for 30 seconds between each addition, until the end point is reached. The end point is determined by the disappearance of the blue colour or by a spot test on a white tile using one drop of an acetic acid solution of potassium ferrocyanide (5 per cent in 10 per cent acetic acid). Place the two spots side by side and note the appearance of a brown fringe.

If all the conditions above mentioned are carefully observed, the precipitate of cuprous oxide will settle readily.

The conditions must be rigidly adhered to in the actual analysis of sugars as in the standardization experiment.

Example.—

Weight of pure glucose in 100 c.c. water 0·8663 gm.

Volume Fehling's solution = 10 c.c.

Approximate volume glucose solution 6·5 c.c.

Readings, 6·05, 6·0, 5·95 c.c.

Hence 10 c.c. Fehling's solution ≡ 6·0 c.c. glucose.

i.e. 1 c.c. Fehling's solution ≡ 0·00519 gm. glucose.

Estimation of Cane Sugar (Volumetric Method).

Weigh out a calculated amount of sucrose to produce an approximately 1 per cent invert sugar solution. Heat the sucrose on the water bath for 20 minutes with 10 c.c. $\frac{N}{2}$ HCl. Cool and neutralize roughly by adding 10 c.c. $\frac{N}{2}$ NaOH solution. Make up to 250 c.c. and titrate as described in the standardization experiments.

Example.—

Weight of sucrose solution 5·1566 gms.

After inversion, made up to 250 c.c.

Volume solution equivalent to 25 c.c. Fehling's solution = 13·2 c.c.

1 c.c. Fehling solution $\equiv$ 0·00516 gm. glucose

$= \frac{19}{20} \times$ 0·00516 gm. sucrose.

Percentage sucrose $= \frac{19}{20} \times 0{\cdot}00516 \times 25 \times \frac{250}{13{\cdot}2} \times \frac{100}{5{\cdot}1566}$.

$= 45{\cdot}01$.

Estimation of Cane Sugar (Gravimetric Method).

A known volume of the invert solution is mixed with excess of Fehling's solution and the mixture heated for 12 minutes in a bath of boiling water. The precipitated cuprous oxide is filtered, washed with water, alcohol, and finally, ether, in a Soxhlet tube on asbestos fibre. It is then dried in the steam oven.

N.B.—The Cu_2O must not be left too long in the oven and should be bright red when weighed.

Factor for above conditions.	Glucose.	Sucrose (inverted).
Cuprous oxide	0·5042	0·4790
Copper	0·5684	0·5408
Cupric oxide	0·4535	0·4308

Example.—

Weight of sucrose solution 8·2989 gms.

Inverted and made up to 250 c.c.

4 c.c. sugar solution run into 10 c.c. Fehling's solution.

Weight of Soxhlet tube and Cu_2O . .	8·0584 gm.
Soxhlet tube	7·9658 ,,
Cu_2O	0·0926 ,,

$$\text{Percentage sucrose } \frac{0{\cdot}0926 \times 0{\cdot}479 \times 250 \times 100}{4 \times 8{\cdot}2989}$$

$$= 33{\cdot}3$$

Estimation of Maltose.

1. Maltose reduces Fehling's solution, but this reduction is not complete. Hence, the sugar must be inverted before estimation.

2. One gm. maltose has the same reducing power as 0·62 gm. glucose.

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

From the above equation 1 gm. maltose gives 1·052 gm. glucose.

After inversion, one gm. maltose has an increased reducing power.

1 gm. maltose $\equiv$ 1·052—0·62 = 0·432 gm. glucose.

i.e. 1 gm. glucose $\equiv$ 2·32 gms. maltose.

The titration result as glucose must be multiplied by the factor 2·32 for conversion to maltose.

Analysis of Sugar Mixtures.

Browne ["J. Amer. Chem. Soc." 28, 439].

Using Fehling's solution, for the same weight of reduced copper produced, reducing sugars bear a constant ratio to one another. The polarization of a sugar, adopting the saccharimeter (Ventzke) method, is equal to its percentage multiplied by a polarization factor found by dividing the specific rotation of the sugar by the specific rotation of pure dextrose (66·5).

A 200 mm. tube is used and a normal weight 26·048 gms. sugar made up.

Let x = percentage of sugar A
y = ,, ,, B
a = dextrose ratio of A
b = ,, ,, B
R = percentage of total reducing sugars as dextrose.

(1) . . . . $ax + by = R$

Let α = polarization factor of A
β = ,, ,, B
P = polarization (Ventzke) of the mixture.

(2) . . . . $ax + \beta y = P$

whence $$x = \frac{bP - \beta R}{ab - a\beta}$$

and $$y = \frac{R - ax}{b}.$$

The above equations can be used in the analysis of mixtures of reducing sugars.

Levulose and Dextrose.—Dextrose ratio of levulose = 0·915.

Polarization factor of levulose (10 per cent solution) at 20° C. = $-\frac{90 \cdot 18}{66 \cdot 5} = -1 \cdot 356$.

Polarization factor of dextrose = $\frac{52 \cdot 74}{66 \cdot 5} = 0 \cdot 793$.

whence the following formulæ may be used :—

(1) Percentage of levulose (at 20°) = $\frac{0 \cdot 793\ R - P}{2 \cdot 08}$

(2) Percentage of dextrose (at 20°) = R − 0·915 L

Value of denominator in (1)

15°	2·12
25°	2·04
30°	2·00

Dextrose ratio of invert sugar is 0·958.

,, equivalent of inverted sucrose solution, 1 part dextrose ≡ 0·993 parts sucrose.

Dextrose and Galactose.—Dextrose ratio of galactose = 0·898.

Polarization factor of galactose (20°) = 1·21,

whence, percentage dextrose = $\frac{1 \cdot 21\ R - 0 \cdot 898\ P}{0 \cdot 498}$

and percentage galactose = $\frac{R - D}{0 \cdot 898}$.

Levulose and Galactose.—

$$\text{Percentage levulose } \frac{1{\cdot}21\ \mathrm{R} - 0{\cdot}898\ \mathrm{P}}{2{\cdot}324}$$

$$\text{,, galactose } \frac{\mathrm{R} - 0{\cdot}915\ \mathrm{L}}{0{\cdot}898}.$$

Dextrose, Levulose, and Sucrose.—

The polarization is expressed by

$$\mathrm{S} + 0{\cdot}793\ \mathrm{D} - 1{\cdot}356\ \mathrm{L} = \mathrm{P}\ (25°).$$

Letting S = the percentage of sucrose obtained by the method of Clerget (rotation before and after inversion),

$$\text{Percentage of levulose} = \frac{0{\cdot}793\ \mathrm{R} + \mathrm{S} - \mathrm{P}}{2{\cdot}08}$$

$$\text{,, dextrose} = \mathrm{R} - 0{\cdot}915\ \mathrm{L}$$

Glucose, Maltose, and Dextrin.—Method of Allen. [Allen's "Commercial Organic Analysis," 1901, I, 365.]

$[\alpha]_D$ glucose = 52·7.
,, maltose = 139·2.
,, dextrin = 198·0.

Copper reducing power of glucose = 1.
,, ,, ,, ,, maltose = 0·62.
,, ,, ,, ,, dextrin = 0.

Allen makes use of the following equations :—

$g + m + d$ = total weight of sugar = O

$g + 0{\cdot}62\ m$ = K (copper reducing power)

$52{\cdot}7\ g + 139{\cdot}2\ m + 198\ d = 100$ S (specific rotation)

whence

$$m = \left(\mathrm{S} - \frac{52{\cdot}7\ \mathrm{K} + 198\ (\mathrm{O} - \mathrm{K})}{100}\right) \div 0{\cdot}313$$

$$g = \mathrm{K} - 0{\cdot}62\ m$$

$$d = \mathrm{O} - (g + m)$$

If *dextrose* and *levulose* occur together in solution, they may be separated by precipitating the sugars as lead compounds with ammoniacal lead acetate.

On passing a current of CO_2 through a suspension of the lead compounds, that of dextrose is decomposed. The residue

containing the lead salt of levulose may then be removed and decomposed with sulphuretted hydrogen.

Sucrose is unacted upon by ammoniacal lead acetate.

Glucose, Sucrose, and Maltose.—Advantage is here taken of the fact that sucrose is inverted by citric acid, whereas maltose is not so acted upon.

Let x = reduced copper equivalent of the sugars, before inversion.

y = the equivalent after inversion with citric acid.

z = the equivalent after inversion with hydrochloric acid.

The amounts of sugars may then be found by using the following equations :—

(a) glucose = x − (maltose × 0·62)

(b) sucrose = (y − x) × 0·95

(c) maltose = (z − y) × 2·32.

Estimation of Sugars by Pavy's Solution.

This solution contains ammonia which dissolves the cuprous oxide. The end point is thus made clearer.

Preparation.—A. Dissolve 8·32 gms. $CuSO_4$ in a litre of water.

B. Dissolve 40·8 gms. Rochelle salt, 40·8 gms. NaOH in 600 c.c. ammonia (0·88) and make up to a litre with water.

Standardize this solution made up of equal volumes of A and B with a known glucose solution.

Fifty c.c. are equivalent to about 0·025 gms. of glucose.

It is necessary that the operation be carried out rapidly or the ammonia may be driven off and the Cu_2O precipitated.

The Pavy solution must be boiling all the time to prevent air entering the narrow necked Erlenmeyer flask. The solution of Cu_2O is oxidized by air.

A suitable method is to take an Erlenmeyer flask provided with a cork bored with two holes. Through one hole is introduced the nozzle of the burette and through the other an outlet tube for steam. Boil the solution over a small flame and to prevent bumping introduce a small piece of porous porcelain.

Estimation of a Mixture of Saccharose, Dextrose, and Levulose.

F. G. Wiechmann ["Chem. News," 66, 237, 249].

The method to be described involves three analytical operations: two gravimetric, and one optical, determinations.

An amount of the sample equal to 10 gms. of dry substance is weighed out, placed in an accurately graduated 100 c.c. flask, dissolved in water and made up to the mark with distilled water.

Optical Examination.—Some of the solution is placed in a water jacketed polarization tube provided with a thermometer, and a reading is taken in the polarimeter at 20°. The reading thus made must be reduced to the basis of one made in a 100 mm. tube, and, if a sugar scale has been used for the observation, the reading must be transformed into circular degrees. With a polarimeter using 26·048 gms. as the normal weight the factor 0·346 is used for the sodium ray.

Gravimetric Estimation before Inversion.—10 c.c. of the solution are made up to 150 c.c. and of this 24·4 c.c. (= 0·1628 gm. dry substance) is taken. 50 c.c. of Fehling's solution is heated to boiling, the sugar solution is added, and the mixture boiled for 3 minutes. After diluting the mixture with cold water, previously boiled, the cuprous oxide is collected on a weighed Gooch crucible and washed with boiling water, alcohol, and finally ether. The weighed precipitate is calculated to its equivalent of metallic copper, and from this figure the corresponding amount of saccharose can be ascertained. The total reducing sugars are calculated by adding $\frac{1}{2}\frac{1}{0}$ to the saccharose value indicated.

Gravimetric Estimation after Inversion.—50 c.c. is heated on the water bath with 4 c.c. of HCl (sp. gr. 1·20) for 5 minutes at 67°. The flask is then removed, and after cooling to the original temperature the contents are made up to 100 c.c. of this solution, 20 c.c. is neutralized exactly with sodium

carbonate and made up to 150 c.c.; of this solution 24·4 c.c. (= 0·1628 gm. dry substance) is taken and treated with alkaline copper solution. The result expresses the total sugars as saccharose. If now the previously found saccharose value is deducted, the difference will represent the actual amount of cane sugar. As the specific rotation powers of saccharose, dextrose, and levulose are known, the operator will now be in possession of all the data required for an algebraic calculation of their percentages.

Allihn's Method for Estimation of Glucose.

["J. pr. Chem.," (2), 22, 46, and "Bull. 107 (revised), U.S. Bur. Chem.," 49.]

Reagents.—

Copper sulphate solution.—Dissolve 34·639 gms. $CuSO_4 5H_2O$ in water and dilute to 500 c.c.

Alkaline-tartrate solution. — Dissolve 173 gms. Rochelle salt and 125 gms. of potassium hydrate in water and dilute to 500 c.c.

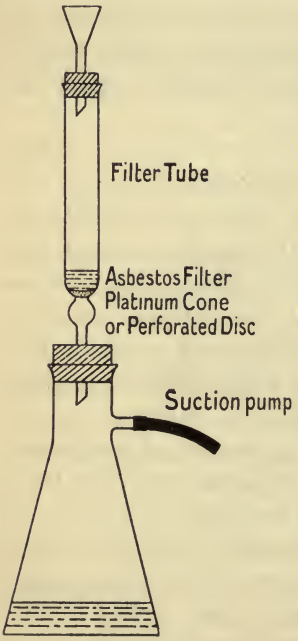


Fig. 44.

Method.—Place 30 c.c. copper solution and 30 c.c. of the alkaline-tartrate solution with 60 c.c. water in a beaker and boil. Add 25 c.c. of the sugar solution containing not more than 1·0 gm. of glucose in 100 c.c. solution and boil for exactly 2 minutes with the beaker covered. Filter immediately through an asbestos filter tube without any dilution using suction (Fig. 44).

Provide the tube with a detachable funnel during filtration, so that none of the precipitate accumulates near the top where it could be removed by the cork during the reduction of the cuprous oxide. Wash the precipitate in the filter with hot water, alcohol, and

finally ether. After being dried, connect the tube with an apparatus supplying a continuous current of dry hydrogen, gently heat until the cuprous oxide is completely reduced to the metallic state, cool in the current of hydrogen and weigh (Fig. 45).

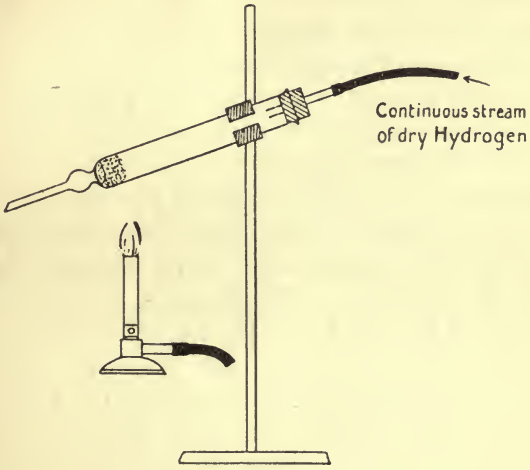


FIG. 45.

All air must be expelled from the tube by hydrogen before heating, otherwise there is danger of an explosion.

Direct weighing of Cuprous Oxide.—Wash and dry the precipitate in the filter tube (or Gooch crucible) as directed above.

Dry for 30 minutes in a water oven at 100° C.; cool and weigh.

This process is satisfactory when dealing with pure substances, but is less accurate when determining impure products. The cuprous oxide is then contaminated with mineral and organic matter.

Thiocyanate Method of Determining the Copper.

Volhard-Pflüger ["Pflüger's Arch.," 69, 423].

Solutions required are:—

(1) Decinormal silver nitrate.
(2) Decinormal ammonium thiocyanate.
(3) Saturated solution of sulphur dioxide in water.
(4) Nitric acid (sp. gr. 1·2) free from nitrous acid.
(5) Normal sulphuric acid.
(6) Saturated solution of ferric alum in water.

The cuprous oxide is dissolved out of the filter tube with nitric acid after the approximate weight of oxide has been determined by weighing. Slight excess of the sulphuric acid is added and the whole is evaporated to dryness. The residue is dissolved in water in a 300 c.c. flask, and sodium carbonate is added to the point of turbidity. Fifty c.c. of the sulphurous acid solution are now added and the mixture boiled for one minute. Now, thiocyanate is added until excess of about 5 c.c. above that required to precipitate the copper as cuprous thiocyanate. The mixture is cooled, made up to 300 c.c., shaken, filtered through a dry filter paper, and 100 c.c. of the clear filtrate taken. This is diluted with 100 c.c. water; 50 c.c. of nitric acid and 10 c.c. of the alum solution are added and the mixture titrated with silver nitrate until the red colour disappears. Titrate back the excess of silver nitrate with thiocyanate until a pink colour appears.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiocyanate} \equiv 6{\cdot}357 \text{ mg. copper.}$$

Let x = number c.c. of thiocyanate added to the 300 c.c., y = number c.c. of $AgNO_3$ added to 100 c.c., z = number c.c. thiocyanate to titrate excess of y, then total mg. copper = $6{\cdot}357\ (x + 3z - 3y)$.

Now refer to Allihn's table.

ALLIHN'S TABLE FOR DETERMINING GLUCOSE. (ABRIDGED.)

WEIGHTS IN MILLIGRAMS.

Cu.	Cu_2O.	Glucose.	Cu.	Cu_2O.	Glucose.	Cu.	Cu_2O.	Glucose.
11	12·4	6·6	165	185·8	84·3	320	360·3	167·5
15	16·9	8·6	170	191·4	86·9	325	365·9	170·3
20	22·5	11·0	175	197·0	89·5	330	371·5	173·1
25	28·1	13·5	180	202·6	92·1	335	377·2	175·9
30	33·8	16·0	185	208·3	94·7	340	382·8	178·7
35	39·4	18·5	190	213·9	97·3	345	388·4	181·5
40	45·0	20·9	195	219·5	100·0	350	394·0	184·3
45	50·7	23·4	200	225·2	102·6	355	399·7	187·2
50	56·3	25·9	205	230·8	105·3	360	405·3	190·0
55	61·9	28·4	210	236·4	107·9	365	410·9	192·9
60	67·6	30·8	215	242·1	110·6	370	416·6	195·7
65	73·2	33·3	220	247·7	113·2	375	422·2	198·6
70	78·8	35·8	225	253·3	115·9	380	426·7	200·8
75	84·4	38·3	230	258·9	118·5	385	433·5	204·3
80	90·1	40·8	235	264·6	121·2	390	439·1	207·1
85	95·7	43·4	240	270·2	123·9	395	444·7	210·0
90	101·3	45·9	245	275·8	126·6	400	450·3	212·9
95	107·0	48·4	250	281·5	129·2	405	456·0	215·8
100	112·6	50·9	255	287·1	131·9	410	461·6	218·7
105	118·2	53·5	260	292·7	134·6	415	467·2	221·6
110	123·8	56·0	265	298·3	137·3	420	472·9	224·5
115	129·6	58·6	270	304·0	140·0	425	478·5	227·5
120	135·1	61·1	275	309·6	142·8	430	484·1	230·4
125	140·7	63·7	280	315·2	145·5	435	489·7	233·4
130	146·4	66·2	285	320·9	148·3	440	495·4	236·3
135	152·0	68·8	290	326·5	151·0	445	501·0	239·3
140	157·6	71·3	295	332·1	153·8	450	506·6	242·2
145	163·2	73·9	300	337·8	156·5	455	512·3	245·2
150	168·9	76·5	305	343·4	159·3	460	517·9	248·1
155	174·5	79·1	310	349·0	162·0	463	521·3	249·9
160	180·1	81·7	315	354·6	164·8			

Method of Bertrand.

["Bull. Soc. Chim.," 35, 1285.]

Reagents :—

1. Dissolve 40 gms. pure $CuSO_4 . 5\ H_2O$ in a litre of water.

2. Dissolve 200 gms. Rochelle salt and 150 gms. sodium hydrate in sticks in a litre of water.

Method.—20 c.c. of the sugar solution containing not more than 0·100 gm. of reducing sugar are placed in a 150 c.c. Erlenmeyer flask and 20 c.c. each of solutions 1 and 2 are added.

Heat to gentle boiling for 3 minutes exactly. The precipitate of cuprous oxide is washed with distilled water and the reduced copper determined by the volumetric permanganate method.

Transfer the asbestos film to a beaker, add 30 c.c. of hot water and heat thoroughly the precipitate and asbestos. Rinse the crucible with 50 c.c. of a hot saturated solution of ferric sulphate in 20 per cent sulphuric acid receiving the rinsings in a beaker containing the precipitate. When the oxide has dissolved, wash the solution into a large Erlenmeyer flask and immediately titrate with standard permanganate solution.

One c.c. permanganate should equal 0·01 gm. copper. In order to standardize the permanganate, make six or more determinations with the same sugar solution, titrating one-half of the precipitations and determining the copper in the others by reduction. (See Allihn's method.)

$$Fe_2(SO_4)_3 + Cu_2O + H_2SO_4 = 2FeSO_4 + 2CuSO_4 + H_2O$$

Hence 1 c.c. $\frac{N}{10}$ $KMnO_4 \equiv 0{\cdot}00636$ gm. copper.

BERTRAND'S TABLE FOR DETERMINING INVERT SUGAR, GLUCOSE, GALACTOSE, MALTOSE, AND LACTOSE. (ABRIDGED.)

Milligrams of Sugar.	Milligrams of Copper Corresponding to				
	Invert Sugar.	Glucose.	Galactose.	Maltose.	Lactose.
10	20·6	20·4	19·3	11·2	14·4
15	30·5	30·2	28·6	16·7	21·4
20	40·4	40·1	37·9	22·2	28·4
25	49·8	49·6	47·0	27·7	35·2
30	59·3	59·1	56·2	33·3	42·1
35	68·5	68·3	65·0	38·7	48·7
40	77·7	77·5	73·9	44·1	55·4
45	86·5	86·4	82·5	49·5	61·9
50	95·4	95·4	91·2	55·0	68·5
55	104·0	104·1	99·7	60·3	74·9
60	112·6	112·8	108·3	65·7	81·4
65	120·9	121·3	116·6	71·1	87·7
70	129·2	129·8	125·0	76·5	94·1
75	137·2	137·9	133·1	81·8	100·4
80	145·3	146·1	141·3	87·2	106·7
85	153·2	154·0	149·4	92·6	112·9
90	161·1	162·0	157·6	98·0	119·1
95	168·8	169·9	165·6	103·2	125·2
100	176·5	177·8	173·6	108·4	131·4

Wiechmann [" Zeit. Ver. deut. Zuckerind.," 1907, 65] proposes the following procedure for the examination of liquid sugar products :—

Twenty-six gms. of the syrup are dissolved in water in a 100 c.c. flask, clarified with basic lead acetate, excess of lead being precipitated by 10 per cent sodium chloride or sulphate ; the solution is made up to 100 c.c., shaken and filtered.

1. *Total Sugar.*— 50 c.c. of this solution are inverted by 5 minutes at 69° with 5 c.c. HCl (sp. gr. 1·188) ; 50 c.c. of this are diluted to 1000 c.c., and 25 c.c. of this last solution corresponding to 0·1625 gm. syrup are neutralized with 25 c.c. of dilute sodium carbonate (1·7 gm. in a litre) ; 50 c.c. of Fehling's solution are added, the mixture is heated to boiling in about 4 minutes, kept boiling for 3 minutes, and the cuprous oxide filtered on an asbestos filter, weighed as such and multiplied by 0·888 to give the equivalent amount of copper.

2. *Reducing Sugar.*—4 c.c. of the clarified solution are made up to 100 c.c.; 50 c.c. of this are boiled with 50 c.c. of Fehling's solution as above described. The difference in the two estimations represents the real amount of sucrose present.

Estimation of Sugars with Mercury Solutions.

1. Knapp ("Zeit. anal. Chem.," 9, 395).

The solution proposed by the author is prepared by dissolving 10 gms. of pure mercuric cyanide in water, adding 100 c.c. of sodium hydroxide solution of 1·145 sp. gr. and making up to a litre.

In making the determination, 100 c.c., standardized against a known weight of pure sugar, is heated to boiling, and the sugar solution (0·5 per cent) is run in as quickly as possible from a burette until a drop of the filtered solution shows upon acidifying with acetic acid, no coloration with ammonium sulphide. The amount of sugar is calculated in the same way as described under Soxhlet's volumetric method with Fehling's solution.

The end reaction is uncertain; hence the process is but little used.

2. Sachsse ["Zeit. Ver. deut. Zuckerind.," 26, 872].

The solution is prepared by dissolving 18 gms. of pure dry mercuric iodide in a solution containing 25 gms. of pure potassium iodide. A solution of 80 gms. of potassium hydrate is added and the volume made up to a litre with water.

The end point of this reaction is determined by treating a drop of the supernatant liquid with a very alkaline solution of stannous chloride.

Forty c.c. of the iodide solution are boiled in a basin, and a standard solution of pure sugar gradually added until a drop shows no coloration with the indicator.

Estimation of Sugars.

Cane Sugar $[a]_D = 66{\cdot}5$.

1. By specific gravity of solution.

For complete tables see "Handbook of Sugar Analysis," C. A. Browne; "Commercial Organic Analysis," Allen.

2. By weighing as such.

3. By fermentation.

The sugar is mixed with yeast and placed in an apparatus such as is employed in the analysis of carbonates. The mixture is incubated for a few hours at 20°-30°, and the dissolved carbon dioxide is swept out by a current of dry air before weighing.

Weight of $CO_2 \times 0{\cdot}95$ = weight of sucrose fermented.

Or, the alcohol produced may be estimated by distillation.

Weight of alcohol $\times 1{\cdot}96$ = weight sucrose.

4. By its reducing action after inversion (described).

5. By its rotatory power (described).

Invert sugar in raw sugar can be estimated by Fehling's method.

Maltose $[a]_D = 138°$.

1. 1 gm. maltose in 1 per cent solution $\equiv$ 197·6 c.c. of Sachsse's solution.

2. Method of A.O.A.C.—Place 50 c.c. of the mixed copper reagent in a beaker and heat to the boiling-point. While boiling briskly add 25 c.c. of maltose solution, containing not more than 0·250 gm. of maltose and boil for 4 minutes. Filter immediately through asbestos and ascertain the amount of copper reduced as in the method already described. Obtain the weight of maltose equivalent to the weight of copper found from the table (Wein).

TABLE FOR ESTIMATION OF MALTOSE. (ABRIDGED.)

WEIGHTS IN MILLIGRAMS.

Copper.	Cuprous Oxide.	Maltose.	Copper.	Cuprous Oxide.	Maltose.
31	34·9	26·1	145	163·2	126·9
35	39·4	29·6	150	168·9	131·4
40	45·0	33·9	155	174·5	135·9
45	50·7	38·3	160	180·1	140·4
50	56·3	42·6	165	185·8	144·9
55	61·9	47·0	170	191·4	149·4
60	67·6	51·3	175	197·0	153·8
65	73·2	55·7	180	202·6	158·3
70	78·8	60·1	185	208·3	162·7
75	84·4	64·5	190	213·9	167·2
80	90·1	68·9	195	219·5	171·6
85	95·7	73·2	200	225·2	176·1
90	101·3	77·7	205	230·8	180·5
95	107·0	82·1	210	236·4	185·0
100	112·6	86·6	215	242·1	189·5
105	118·2	91·0	220	247·7	193·9
110	123·8	95·5	225	253·3	198·4
115	129·6	99·9	230	258·9	202·9
120	135·1	104·4	235	264·6	207·4
125	140·7	108·9	240	270·2	211·8
130	146·4	113·4	245	275·8	216·3
135	152·0	117·9	250	281·5	220·8
140	157·6	122·4			

Lactose $[a]_D = 52{\cdot}7$.

Method of A.O.A.C.—Place 50 c.c. of the mixed copper reagent in a beaker and heat to boiling. Add 100 c.c. of lactose solution (0·3 gm.) and boil for 6 minutes. Filter immediately through asbestos and determine the copper or cuprous oxide. Obtain weight of lactose from table (Soxhlet-Wein.)

TABLE FOR ESTIMATION OF LACTOSE. (ABRIDGED.)

WEIGHTS IN MILLIGRAMS.

Copper.	Lactose.	Copper.	Lactose.	Copper.	Lactose.
100	71·6	205	150·7	305	228·3
105	75·3	210	154·5	310	232·2
110	79·0	215	158·2	315	236·1
115	82·7	220	161·9	320	240·0
120	86·4	225	165·7	325	243·9
125	90·1	230	169·4	330	247·7
130	93·8	235	173·1	335	251·6
135	97·6	240	176·9	340	255·7
140	101·3	245	180·8	345	259·8
145	105·1	250	184·8	350	263·9
150	108·8	255	188·7	355	268·0
155	112·6	260	192·5	360	272·1
160	116·4	265	196·4	365	276·2
165	120·2	270	200·3	370	280·5
170	123·9	275	204·3	375	284·8
175	127·8	280	208·3	380	289·1
180	131·6	285	212·3	385	293·4
185	135·4	290	216·3	390	297·7
190	139·3	295	220·3	395	302·0
195	143·1	300	224·4	400	306·3
200	146·9				

GLUCOSE AS OSAZONE.

Davis and Ling [" J.C.S.," 1904, **85**, 24].

This method is recommended for estimating the products of the action of malt on starch.

Twenty c.c. of solution containing 2 to 3 per cent starch products are mixed with 1·5 c.c. of 50 per cent acetic acid and 1 c.c. of phenylhydrazine. Heat for not more than an hour on a water bath and filter the concentrated liquid through a Gooch. Wash the residue with 20 to 30 c.c. of boiling water keeping the total filtrate less than 50 c.c. Dry in a steam oven and weigh.

0·1 gm. glucose = 0·0505 gm. osazone.

Estimation of Glycogen.

The sample is hydrolyzed with dilute hydrochloric acid on a water bath for three hours, neutralized, and titrated with Fehling's solution.

Glucose × 0·9 = glycogen.

Estimation of Pentoses.

In the determination of these sugars, use is made of the fact that they yield furfural when distilled with hydrochloric acid. Furfural may be estimated with ammonia, phenylhydrazine, or by phloroglucinol. The latter method is due to Tollens and Kröber ["J. Land.," 1900, 48, 355; 1901, 49, 7], and will be here described.

Two to five gms. of the substance are placed in a 300 c.c. distillation flask with 100 c.c. of hydrochloric acid (sp. gr. 1·06), and the whole heated at 100° C. on a bath of fused Rose's alloy. The distillate is collected in a graduated vessel, and when 30 c.c. have collected, a similar volume of hydrochloric acid is added to the distillation flask by means of a tap funnel. This operation is repeated nine to twelve times, until the distillate gives no coloration with aniline acetate paper.

The united distillate is placed in a 500 c.c. beaker with twice the theoretical quantity of phloroglucinol solution (see below).

The solution is made up to 400 c.c. with hydrochloric acid (1·06) and allowed to stand for some hours, when the supernatant liquid is tested for free furfural.

The mixture is filtered through a tared Gooch and the residue washed with 150 c.c. of water keeping the crucible full during this operation. The crucible and its contents are then dried for 4 hours in a steam oven, cooled in a desiccator and reweighed.

Tables and formulæ are given for the conversion of phloroglucide into pentose and pentosan.

Let a = weight of phloroglucide.

If a is less than 0·03 gm.,

then, Furfural = $(a + 0·0052) \times 0·5170$ gm.
Pentose = $(a + 0·0052) \times 1·0170$,,
Pentosan = $(a + 0·0052) \times 0·8949$,,

If a is more than 0·300 gm.,

then, Furfural = $(a + 0·0052) \times 0·5180$ gm.
Pentose = $(a + 0·0052) \times 1·0026$,,
Pentosan = $(a + 0·0052) \times 0·8824$,,

The factor 0·0052 is obtained, as 5·2 mg. of phloroglucide remain dissolved in 400 c.c. of acid solution.

See also Böddener and Tollens ["J. Land.," 1910, **58**, 232].

TABLE BY KRÖBER. (ABRIDGED.)

Weights in Grams.

Phloroglucide.	Furfural.	Pentose.	Pentosan.
0·03	0·0182	0·0358	0·0315
0·04	0·0235	0·0459	0·0404
0·05	0·0286	0·0559	0·0492
0·06	0·0338	0·0660	0·0581
0·07	0·0390	0·0761	0·0670
0·08	0·0442	0·0861	0·0758
0·09	0·0494	0·0962	0·0847
0·10	0·0546	0·1063	0·0935
0·11	0·0598	0·1163	0·1023
0·12	0·0650	0·1263	0·1111
0·13	0·0702	0·1364	0·1201
0·14	0·0754	0·1464	0·1288
0·15	0·0805	0·1565	0·1377
0·16	0·0857	0·1665	0·1465
0·17	0·0909	0·1766	0·1554
0·18	0·0961	0·1866	0·1642
0·19	0·1013	0·1965	0·1729
0·20	0·1065	0·2065	0·1817
0·21	0·1116	0·2164	0·1904
0·22	0·1168	0·2264	0·1992
0·23	0·1220	0·2364	0·2081
0·24	0·1271	0·2463	0·2168
0·25	0·1323	0·2563	0·2256
0·26	0·1374	0·2662	0·2342
0·27	0·1426	0·2761	0·2429
0·28	0·1478	0·2861	0·2517
0·29	0·1529	0·2960	0·2605
0·30	0·1581	0·3060	0·2693

Preparation of Phloroglucinol Solution.—["Bull. 107 (revised) U.S. Bureau of Chemistry," 54.]

Commercial phloroglucinol may contain diresorcin which is tested for by adding a few drops of acetic anhydride and concentrated sulphuric acid to a small quantity of the sample. If diresorcin is present, a violet colour is produced on heating.

The impurity is separated as follows :—

Treat 11 gms. of the phloroglucinol with 300 c.c. hydrochloric acid (sp. gr. 1·06) adding the solid a small quantity at a time. Stir until nearly dissolved, and pour into cold hydrochloric acid (1·06) until the volume is 1500 c.c. Allow to stand for several days when the diresorcin crystallizes out. A yellow colour produced does not affect the utility of the solution, which must be filtered immediately before its use.

Aniline acetate is prepared according to Tollens ["Land. Vers-Stat.," **39**, 425] in the following manner :—

Shake up equal volumes of aniline and water in a test tube and add glacial acetic acid until the mixture of liquids becomes clear.

Colorimetric Methods for the Estimation of Carbohydrates.

W. H. Dehn and F. A. Hartmann ["J. Amer. Chem. Soc," 1914, **36**, 403].

The method depends on the formation of a red to brown colour when solutions of sugars are heated with a sodium carbonate solution of picric acid. The authors show that great accuracy can be obtained in the case of the commoner sugars.

The advantages claimed for the method include rapidity of estimation and cheapness of reagents.

The original paper contains many references to colorimetric methods of sugar analysis.

Estimation of Starch.

There are several methods for the determination of starch in crude samples, each having certain advantages, according to the origin of the commercial product.

Starch is usually, however, estimated by extraction, the extract being hydrolyzed into known sugars which are then determined in the usual manner. It may be hydrolyzed by acids or by ferments.

Hydrolysis by Acids.—Dilute solutions of strong acids hydrolyze starch under easier conditions than solutions of weak acids. Thus, a dilute hydrochloric acid solution effects the change at a temperature less than 100° C., whereas weak acids require higher temperatures and also that the operation be carried out under pressure.

Method of Sachsse, modified by the A.O.A.C. ["Bull. 107 (revised) U.S. Bur. of Chem.," 53].

Three gms. of the sample are treated with 50 c.c. of cold water for an hour with occasional stirring. The mixture is then filtered, washed with water, and the filtrate made up to 250 c.c. Should difficulty be encountered in obtaining a clear filtrate, 2 c.c. of alumina cream are added. The soluble sugars are estimated before and after inversion.

The insoluble residue is boiled under reflux apparatus for 2½ hours with 200 c.c. water and 20 c.c. hydrochloric acid (sp. gr. 1·125). The mixture is then cooled, nearly neutralized with caustic soda solution, and made up with water to 250 c.c. The contents of the flask are then filtered and the dextrose present determined in an aliquot portion of the filtrate by Allihn's method.

$$\text{Dextrose} \times 0{\cdot}9 = \text{starch}.$$

Hydrolysis by Malt Solution. — Method of Brown. ["Trans. Guiness Research Laboratory," 1903, 1, 79].

Five gms. of the well-powdered sample are taken and the moisture determined.

The starch is then extracted in a modified Soxhlet apparatus with 80 c.c. alcohol (0·920), the contents being

then added to 100 c.c. of water in a beaker and the whole boiled.

The mixture is then cooled to 57° C. and 10 c.c. of malt extract [1] added. After standing for one hour at this temperature the mixture is boiled, filtered into a 200 c.c. flask, the residue washed with water and the liquid made up to the mark with water when cold.

The maltose in solution is estimated by the copper reduction method, when under certain conditions [2] 84·4 parts of maltose are equal to 100 parts of starch.

[1] Digest 10 gms. of fresh, ground malt with 200 c.c. water for two to three hours and filter.

[2] See also Brown, Morris, and Millar ["J.C.S.,' 1897, 71, 94].

DYESTUFFS.

Estimation of Nitro-Compounds.

Knecht ["J. Soc. Dyers and Colourists," 1903, vol. VI. 19].

The reduction of nitro-compounds to amido compounds is quantitative when titanous chloride is used as the reducing medium.

$$-NO_2 + 3H_2 = -NH_2 + 2H_2O$$
$$TiCl_3 + HCl = TiCl_4 + H$$

Each nitro group requires six molecules of titanous chloride for its complete reduction.

Although many nitro-compounds are intensely coloured, they cannot act as their own indicators since the colour vanishes before the end of the reaction.

Nitrobenzene.—A known weight of this substance was sulphonated by heating with about twenty times its weight of fuming sulphuric acid (20 per cent) on a water bath for 2 hours and the following results were obtained :—

Calculated 100. Found (*a*) 99·98, (*b*) 99·60. The method adopted is the indirect one used in the determination of Benzopurpurin 4B. [See determination of Azo-dyes.]

Using this method, the following substances may be thus estimated :—

Picric acid, *p*-nitraniline, nitroso-dimethylaniline.

The latter substance, typifying the nitroso-compounds, can be estimated by direct titration using solutions at a temperature 40°-50°C.

Analysis of Azo-dyestuffs.

1. Reduction with zinc dust and alkali.
   (*a*) *Base volatile.*—In this case the base is separated by steam distillation and conversion into acetyl compound.
   (*b*) *Base non-volatile.*—The base is here extracted with alcohol and subsequently investigated.
2. Witt ["Ber.," 1888, 21, 3471].

One gm. of recrystallized dye is dissolved in about 10 c.c. water at boiling temperature. Treat with 6 c.c. of a solution prepared by the solution of 40 gms. of stannous chloride in 100 c.c. pure hydrochloric acid (sp. gr. 1·19).

The bases are then investigated by the usual qualitative tests.

3. Titration with Titanous Chloride.

Edmund Knecht ["J. Soc. Dyers and Colourists," 1903, vol. VII., xix.].

Most dyestuffs are decolorized by strong reducing agents, either to leuco base or permanently as with the azo colours, and nitro-compounds in acid solution.

A. Müller has given a method for the determination of indigotine by means of sodium hydrosulphite. Stannous chloride does not give quantitative results.

$$C_6H_5N : N . C_{10}H_6 . OH + 2H_2 =$$
$$C_6H_5NH_2 + C_{10}H_6\begin{matrix}OH\\NH_2\end{matrix}.$$

Hence each $-N : N-$ requires $4TiCl_3$ or 4 Fe for its complete reduction.

Storing and standardizing the titanous chloride solution, see Nitro Group, Chap. III.

Soluble Dyes.—A direct titration is carried out, the dye acting as its own indicator.

Use 0·5 gm. dyestuff in 500 c.c. and use 100 c.c. of the solution for the determination.

Example :—

Crystal scarlet 6R.

$C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$ (from *a*-naphthylamine and G salt).

100 c.c. [containing 0·1 gm.] were measured out into a conical flask, 10 c.c. concentrated hydrochloric acid added, and the whole boiled for a minute. Volume of titanous chloride 22·6 c.c. required for complete decolorization.

1 c.c. $TiCl_3 \equiv 0{\cdot}0015797$ gm. Fe.

502 gms. colour $\equiv$ 224 gms. Fe (by theory).

$$\therefore \frac{0{\cdot}0015797 \times 22{\cdot}6 \times 502}{224} = 0{\cdot}08001 \text{ gm. colour.}$$

		Calc.
1 gm. contains 0·8001 gm. or	80·01 per cent	79·96 per cent
Water of crystal. at 140° C.	19·96 ,,	20·04 ,,
Total	99·97 ,,	100·00 ,,

Insoluble Dyes.—In the case of dyestuffs which, like the majority of the benzidine derivatives are thrown out of solution by hydrochloric acid, the reaction is too slow and the end-point is not distinct to admit of exact determinations. In such cases it is best to run in an excess of titanous chloride solution into the boiling solution of the dyestuff, taking the precaution of allowing a gentle current of carbonic acid (from a Kipp generator) to pass into the flask by a tube which reaches nearly to the surface of the liquid.

The reduction is usually accomplished in 2 minutes, when the flask is cooled under the tap without interrupting the current of carbonic acid.

When cold the excess of titanous chloride is estimated as described, by running in iron alum solution of strength nearly equivalent to that of the titanous chloride solution until a drop taken out and spotted on potassium thiocyanide solution just shows a red colour.

By subtracting the number of c.c.'s of the alum solution (or their equivalent in titanous chloride should the two solutions not be of equal strength) from the total number of c.c.'s

of titanous chloride run in, the exact amount of the latter used up in the reduction of the dyestuff is found.

Example :—

Benzopurpurin 4B

$C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2}H_2O$ (potassium salt of the colouring stuff from tolidine and naphthionic acid).

0·5 gm. is dissolved in 500 c.c. distilled water. Of this 100 c.c. are measured into a conical flask and heated to the boil; 10 c.c. concentrated hydrochloric acid and 50 c.c. $TiCl_3$ solution are now added, a current of carbonic acid being passed into the flask. The contents are boiled for one minute and complete reduction takes place. After cooling, the solution requires 22·9 c.c. iron alum solution (equivalent to 21·0 c.c. titanous chloride).

Hence 29·0 c.c. titanous chloride $\equiv$ 0·1 gm. dye.

1 c.c. $TiCl_3 \equiv$ 0·001845 gm. Fe.

756 gms. colour $\equiv$ 448 gms. Fe (by theory).

$$\therefore \frac{0{\cdot}001845 \times 29{\cdot}0 \times 756}{448} = 0{\cdot}09026 \text{ gm. colour.}$$

			Calc.
1 gm. contains 0·9026 gm.	=	90·26 per cent	90·33 per cent
Water of crystallization	=	9·63 ,,	9·67 ,,
		99·89 ,,	100·00 ,,

Sisley ["Bull. Soc. Chim.," 1901, 862], has shown that azo-dyes contain water of crystallization when crystallized from their aqueous solutions. Hence it is important to ascertain the amount of water in a dyestuff by heating a weighed quantity to constant weight in an oven at 105° C.

ESTIMATION OF INDIGO.

C. Rawson ["Chem. News," 1881, **52**, 7, and "J. Soc. Dyers and Colourists" (4), 1].

Classification :—

(i) Indigo dissolved by sulphuric acid.

(ii) Indigotin estimated by sublimation.

(iii) Indigo reduced to indigo white in alkaline solution.

I.—Solution in Sulphuric Acid.

1 gm. of finely powdered indigo is intimately mixed in a small mortar with its own weight of ground glass. The mixture is gradually and carefully added, during constant stirring with a glass rod to 20 c.c. of concentrated sulphuric acid (1·845 sp. gr.) contained in a cylindrical porcelain crucible (C. 1½ oz.); the mortar is rinsed out with a little powdered glass, which is added to the contents of the crucible, and the whole is exposed in a steam oven for a period of 1 hour to a temperature of 90° C. The sulphindigotic acid thus formed is diluted with water and made up to 1 litre.

The subsequent oxidation is carried out by permanganate.

About 1 gm. of the sample is dissolved in sulphuric as stated above, diluted to 1 litre and filtered; 50 c.c. of the filtrate are measured into a porcelain dish, to which are added 250 c.c. distilled water. To this solution a standard permanganate (0·5 gm. per litre) is run in from a burette, until the liquid which at first takes a greenish tint changes to a light yellow.

$$5\ C_8H_5NOSO_3 + K_2Mn_2O_8 + 3H_2SO_4 = 5\ C_8H_5NO_2SO_3 + K_2SO_4 + 3H_2O + 2MnSO_4.$$

Hence 316 parts of permanganate are equivalent to 655 parts of indigotin.

Notes.—1. With a strong solution of indigotin, the theoretical amount of permanganate is decolorized.

2. In order to obtain comparative results it is necessary that dilute solutions are used, as the reaction which takes

place is not strictly in accordance with the above equation. The strength of the permanganate should be found by treating a known weight of pure indigotin as above (0·5 gm.).

Potassium Ferricyanide Process.—Ullgreen ["J.C.S.," 1865, 223].

One gm. of indigo is dissolved in less than 10 gms. of sulphuric acid at a temperature lower than 50°, and diluted to a litre; 10 c.c. are taken and mixed with 20 c.c. of a cold saturated solution of sodium carbonate and 1 litre of distilled water in a porcelain basin; a weak solution of potassium ferricyanide (2·5115 gms. per litre) is gradually added with constant stirring.

Notes.—Impurities do not interfere with this process so much as in the permanganate method, but the results are too high. The solutions must be very dilute, and hence the end point is indistinct.

Hyposulphite Method.—A. Müller ["American Chemist," 5, 128] recommended the use of a solution of sodium hyposulphite (Na_2SO_2) in order to reduce sulphindigotic acid quantitatively to disulpholeucindigotic acid. This method has been modified by Rawson as follows :—

(*a*) *Preparation of Sodium Hyposulphite.*—A flask of about 100 c.c. capacity is loosely filled with twisted sheet zinc, which is covered with a solution of sodium bisulphite (sp. gr. 1·30). The flask is corked and allowed to stand for about 1 hour, when the bisulphite will be found to have lost the smell of sulphur dioxide. The liquid is now decanted and well mixed in a large flask with 5 litres of distilled water, containing in suspension about 50 gms. of recently slaked lime. The vessel is closed to prevent access of air, and, after allowing the insoluble matter to subside, the clear liquid is syphoned off into a store bottle, the surface being covered with about 100 c.c. of petroleum. The bottle is provided with a cork through which pass two tubes, one of which is in the form of a syphon and is used to fill the burette; the other tube which only just passes through the cork is connected to a coal-gas supply. The bottle is covered with a sheet of black paper.

(*b*) *Standardization of the Solution.*—A standard solution of copper sulphate is prepared by dissolving 1·904 gms. of the crystallized salt in a litre of water containing 100 c.c. of ammonia (sp. gr. 0·880); 50 c.c. of this solution are measured into a wide-mouthed flask (200 c.c.), boiled to expel air and allowed to cool. The flask is provided with a rubber stopper, perforated with four holes, into two of which are fitted two Mohr's burettes, one containing the hyposulphite solution and the other a solution of indigo-carmine. The two other holes serve for the entrance and exit of a current of hydrogen or coal-gas, as the process must be conducted without access of air. The hyposulphite burette is furnished with a perforated cork, through which passes a tube connected to a coal-gas supply; and at the lower extremity a glass tube is joined to it, which is in communication with the store bottle.

The flask containing the copper sulphate solution is attached to the rubber stopper, and air is expelled by means of coal-gas, which should pass through U-tubes of ferrous-hydrate.

The solution of hyposulphite is now run in until the liquid becomes nearly colourless, when a few drops of indigo-carmine are added from the second burette. Finally, a further quantity of hyposulphite is added, until the solution assumes a peculiar brownish-red colour.

By a blank test the amount of hyposulphite needed to decolorize the indigo-carmine is found and is deducted from the total volume used.

The 50 c.c. of copper solution $\equiv$ 0·05 gm. indigotin whence the strength of the hyposulphite in terms of indigotin can be easily calculated.

(*c*) *Titration of Indigo-sulphate.*—About 1 gm. of indigo is dissolved (as stated above) in sulphuric acid. It is diluted to 1 litre and filtered; 50 c.c. are measured into the titration flask, boiled to expel air and allowed to cool. The titration is carried out as in the standardizing of the hyposulphite solution, the indigo when reduced assuming a pale yellow tint.

II.—Sublimation Method.

C. Tennant [" Chem. News," 1884].

About 0·25 gm. powdered indigo, dried at 100°, is weighed into a shallow platinum dish (7 cms. long, 2 cms. wide, 3-4 mm. deep), and spread evenly.

The operation is conducted on an iron plate, which is heated gradually to avoid burning. When the surface of the indigo is covered with a shining mass of crystals, a piece of sheet iron, bent into the form of a low arch, is placed over the dish, and as the temperature rises, the gas is turned down. The tray is again weighed after cooling in a desiccator. The loss in weight is indigotin.

III.—Reduction in Alkaline Solution.

All methods are based on the formation of indigo-white by nascent hydrogen and its subsequent oxidation to indigotin.

Fritzsche's method depends upon the reduction of indigotin in an alkaline alcoholic solution by means of grape sugar. The solution is then exposed to the air when indigotin gradually separates out. Another method is to treat powdered indigo, out of air contact, with a solution of ferrous sulphate and slaked lime. After gently heating, the precipitated matter is allowed to subside; a measured volume of clear liquid is decanted into a beaker, rendered acid and oxidized to indigotin. The precipitate is collected, washed, dried, and weighed.

Reduction by Ferrous Sulphate and Sodium Hydrate.—Crace-Calvert [" Dyeing and Calico Printing," p. 196] devised a reliable method which has been modified by C. Rawson.

One gm. of finely powdered indigo is placed in a flask, with 2 gms. of ferrous sulphate, 5 gms. of sodium hydrate, and about a litre of water. The flask is closed with a cork having three holes, in one of which is fixed a syphon for run-

ning off the reduced indigo; the other holes are used for the entrance and exit of coal-gas or hydrogen.

The mixture is kept at a temperature a little below the boiling-point for 1½ to 2 hours, when the source of heat is removed and the residue is allowed to subside; 500 c.c. are syphoned off, the remainder being accurately measured. The reduced indigo is allowed to oxidize by drawing a current of air through the solution. Add an excess of hydrochloric acid and allow the precipitate to subside; the clear liquid is decanted on to a weighed filter, and the residue washed with hot water. The residue is boiled with alcohol, cooled somewhat, and transferred to the filter, washed with 80 per cent alcohol, dried at 100° and weighed. The result is indigotin.

Reduction by Sodium Hyposulphite and Lime.—C. Rawson ["J. Soc. Dyers and Colourists," (4) 1].

One gm. of powdered indigo is ground into a thin paste with water, and introduced into a flask with 500-600 c.c. of lime water. The flask is provided with a rubber stopper with four holes, in one of which is inserted a syphon closed by a pinch-cock and in another is fixed a funnel provided with a stop-cock. The other two holes serve for the entrance and exit of coal-gas. The flask is connected with a supply of coal-gas, and the contents heated to about 80° C.; 100-150 c.c. of a solution of sodium hyposulphite are now introduced by means of a funnel, and the mixture, which assumes a yellow tint after a few minutes, is kept near the boiling-point for half an hour. After allowing the insoluble residue to subside, 500 c.c. are syphoned off and the remaining liquid accurately measured. The sodium hyposulphite used is five times the strength of the solution previously described.

The 500 c.c. are poured into a conical flask, and a current of air drawn through the liquid for about twenty minutes. An excess of hydrochloric acid is added, when the oxidation to sulphite is complete, to dissolve any carbonate of lime in the precipitate. The latter is collected on a weighed filter, washed with hot water, dried at 100° and weighed. This is indigo-blue and indigo-red. The latter can be dissolved out by alcohol in an extraction apparatus.

Other literature on the subject.—Ullgreen ["Dingl. Poly. J.," 179, 457]; Leuchs ["J. pr. Chem.," 105, 107]; Mohr ["Dingl. Poly. J.," 132, 363]; Ullgreen ["Wagner's J.," 1865, 650].

W. P. Bloxam ["J. Soc. Chem. Ind.," 1906, 25, 735].

One gm. of the sample dried at 110°, is heated in a water oven for half an hour with 2-3 gms. of clean sand and 5 c.c. fuming H_2SO_4 (20 per cent SO_3). After cooling, the mixture is diluted to 500 c.c. with water; 100 c.c. of this solution are placed in a conical beaker and 100 c.c. of a 45 per cent potassium acetate solution are run in; the contents of the beaker are next heated until complete solution of the precipitate has taken place and then cooled in ice for one hour. The tetrasulphonate separates out and is collected on a filter moistened with a solution prepared by adding 5 c.c. of glacial acetic to 200 c.c. 45 per cent potassium acetate solution and diluting the mixture with 400 c.c. water.

The precipitate is dissolved in hot water, made up to 200 c.c. with water and portions titrated with potassium permanganate or titanium trichloride solutions.

Potassium Permanganate Used.—20 c.c. tetrasulphonate solution are diluted with 80 c.c. water, 0·5 c.c. H_2SO_4 added, and 0·1 per cent potassium permanganate solution run in until the addition of a drop no longer produces a cloud in the yellow liquid. Pure indigotin under these circumstances would require 9·0 c.c. of the permanganate solution.

Titanium Trichloride Used.—25 c.c. tetrasulphonate solution are treated with 1·5 c.c. of a 20 per cent disodium tartrate solution and the mixture titrated at boiling temperature in an atmosphere of CO_2.

OILS, FATS, AND WAXES.

The analysis of an unknown oil has not for its object the separation of individual members, but the determination of certain chemical and physical data which are found to be characteristics of various types of these substances. For example, the iodine value of the oil will give information concerning its drying powers—drying oils having high, and non-drying oils low, iodine values.

Oils are triglycerides of different acids, hence any differences found in them are generally accounted for by the chemical character of the combined acid. An analysis will show whether the acid has a high or low molecular weight, whether it has hydroxy groups in the molecule, and whether it has an unsaturated molecule.

In a mixture of oils the mean molecular weight is determined by the saponification of a certain amount; the proportion of acids of high or low molecular weight by the Reichert-Meissl value, the unsaturation by the iodine value, the number of hydroxy groups by the acetyl value, and free acids by direct titration.

Other determinations sometimes made are density, viscosity, melting-point of solids, heat of combustion, and the Maumené value which depends on a thermal action brought about by mixing a known amount of the oil with sulphuric acid.

In the following pages will be described the methods usually adopted in the determination of :—

(1) The iodine value.
(2) The acid number.
(3) The saponification value.
(4) The acetyl value.
(5) The Reichert-Meissl value.

Unsaturation.

Action of Bromine.—Crossley and Renouf ["Trans. Chem. Soc.," 1909, 648]. Into the flask A (Fig. 46) is placed about 30 c.c. dry chloroform and an accurately weighed quantity (1-1·5 gms.) of the substance to be tested, and the flask stoppered securely with an ordinary cork. The drop-

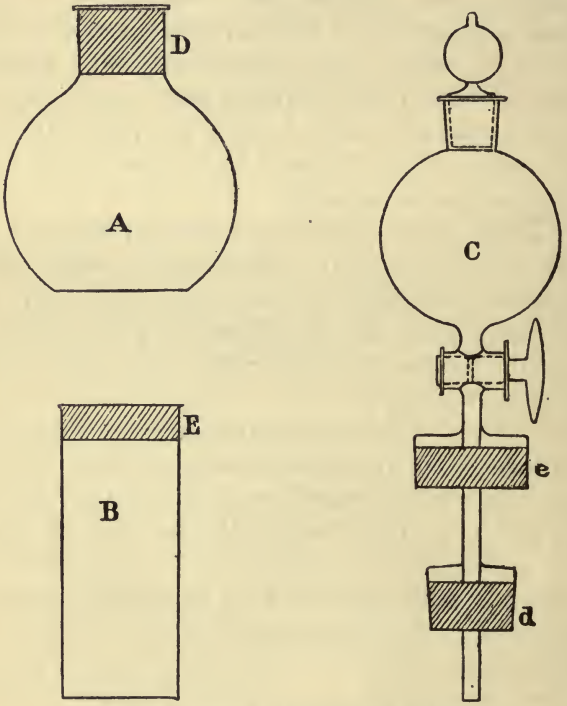


Fig. 46. (From the Chemical Society.)

ping funnel C is then attached to B by the ground glass joint E*e*, and into C is weighed about 25-30 gms. dry chloroform and 3-4 gms. of dry bromine. C is then attached to A by the ground glass joint D*d* and, when the absorption is complete, is again placed in B and reweighed. Any chloroform solution of bromine remaining in the stem of the funnel is prevented from escaping.

A solution of dimethyldihydro benzene in chloroform rapidly decolorized a solution of bromine in the same solvent, and a sharp end-point was noted when one molecule of bromine had been absorbed.

1·0747 absorbed 1·6066 Br. Molecular absorption = 161·4.

C_8H_{12} requires 160 for Br_2 and 320 for Br_4

I.—Iodine Value.

Hübl observed that an alcoholic solution of iodine containing mercuric chloride reacts with the unsaturated portion of acids, both free, and combined in the form of oils and fats.

The "iodine value" is of great importance in the characterization of a fat.

The following solutions are necessary :—

(i) Mix together, about 24 hours before use, in equal volumes, 25 gms. iodine in water, and 30 gms. mercuric chloride in 500 c.c. of 96 per cent alcohol.

(ii) A sodium thiosulphate solution containing 24 gms. of crystallized salt per litre.

(iii) Chloroform or carbon-tetrachloride, which does not absorb iodine.

(iv) Solution of potassium iodide in water (1 : 10).

(v) Solution of starch. Boil up 0·5 gm. starch in suspension with 50 c.c. water.

Standardization of the Thiosulphate.—Make up a potassium bichromate solution containing 3·8657 gms. of pure salt in one litre of water. Place 10 c.c. of the iodide solution (free from iodate) and 5 c.c. concentrated HCl in a stoppered bottle and add 20 c.c. of the bichromate solution. The solution now contains 0·2 gm. free iodine; it is at once titrated against the thiosulphate solution using starch as indicator.

Let x = volume of thiosulphate.

then 1 c.c. thiosulphate $\equiv \frac{0{\cdot}2}{x}$ gms. iodine.

Determination of iodine value :—

Take 0·15 to 0·18 gms. drying oil,
0·2 to 0·3 gms. semi-drying oil,
0·3 to 0·4 gms. non-drying oil,
or 0·8 to 1·0 gms. solid fat,

weighed from a weighing bottle by difference into a tall stoppered bottle containing 500 c.c., and dissolved in 10 c.c. chloroform.

Run in 25 c.c. of the iodine solution. If a clear solution is not obtained add more chloroform, and then stand in a dark place for about 2 hours. The stopper should be moistened with KI solution to prevent loss of iodine by volatilization. If at the end of 2 hours the solution is colourless, a further quantity (25 c.c.) of iodine solution is added to provide ample excess of iodine. Drying oils take 12-18 hours, fats and non-drying oils 6-8 hours for completion of the reaction.

Add 20 c.c. iodide solution and dilute to 400 c.c. with water. A further amount of KI solution is added should a red precipitate of mercuric iodide form.

Now shake with standardized thiosulphate solution until only a faint yellow colour remains.

Complete the titration in the presence of starch solution.

Standardization of Iodine Solution.—Take 25 c.c. of the original iodine solution and titrate with the standard thiosulphate solution.

From the above data the amount of iodine absorbed by the oil is obtained.

The "iodine value" is the percentage of iodine chloride absorbed by the oil in terms of iodine.

Objections to Hübl Process.

P. C. McIlhiney ["J Amer. Chem. Soc.," 1899, 21, 1085].

1. The solution of iodine and mercuric chloride is not a stable one. Several hours must be devoted to the preparation of this reagent before the analysis proper can be carried on.

2. The reaction between the reagent and oil is not instantaneous. With drying oils probably 18 hours are required. This delays the analysis.

3. The process does not distinguish between iodine absorbed by addition and that absorbed by substitution. In the case of glycerides this is not so serious a defect as in the case of hydrocarbon oils and resins. Hence, rosin and linseed oil may give the same Hübl figures although the behaviour towards halogen is essentially different.

Method of Wij.

["Zeit. anal. Chem.," 1898, 277, and "Zeit. unters Nahr. Genussm.," 1902, 497].

Iodine Solution.—Dissolve[1] 7·9 gms. iodine chloride in 200 c.c. glacial acetic acid. Dissolve in a similar volume of acetic acid, 8·7 gms. of powdered iodine and gently warm. Mix the two solutions in a 1000 c.c. flask and make up to the mark with glacial acetic acid.

This solution is standardized by mixing 20 c.c. with 10 c.c. of the 10 per cent KI solution, and titrating the free iodine after making up to 400 c.c. with water, with thiosulphate (y c.c.).

$$1 \text{ c.c. thiosulphate} \equiv \frac{0{\cdot}2}{x} \text{ gm. iodine, see above,}$$

$$\text{hence 1 c.c. iodine solution} = \frac{0{\cdot}01\,y}{x} \text{ gm. iodine.}$$

Determination of the Iodine Value.—Place a weighed quantity of oil or fat (see previous method) with 10 c.c. carbon-tetrachloride and 25 c.c. iodine solution in a stoppered bottle. Set aside for 2 hours in a dark place. Add 10 c.c. KI solution and make up with water to 400 c.c.

Titrate with thiosulphate solution.

Deduce iodine value as in previous method.

[1] Or, by dissolving 13 gms. of iodine in a litre of glacial acetic acid and passing in chlorine until the titration value has doubled. This point is shown by a change in colour.

Method of Schweitzer and Lungwitz ["J. Soc. Chem. Ind.," 1895, 14, 130].

A quantity of the oil to be analysed is weighed into a glass-stoppered bottle, 10 c.c. of CCl_4 added to dissolve the oil, and 20 c.c. $\frac{N}{3}$ bromine in CCl_4 added from a pipette provided with a rubber tube. Another pipette full of solution should be added to 10 c.c. CCl_4 and this blank titrated with thiosulphate to find the strength of the bromine solution.

The test itself need be allowed to stand only one or two minutes before adding 20-30 c.c. of 10 per cent KI solution, the amount added depending upon the excess of bromine present.

In order to prevent any loss of bromine or hydrobromic acid which would probably occur on removing the stopper of the bottle, a short piece of wide rubber tubing, of the sort used in Gooch crucibles, is slipped over the lip of the bottle so as to form a well around the stopper. It is advisable, also, to cool the bottle by setting it in a freezing mixture in order to produce a lowering of the pressure in the interior.

Into the well formed by the rubber tubing is poured the solution of KI and the stopper opened slightly. If the bottle has been cooled the iodide solution is sucked into the bottle, otherwise air passes out of the bottle and is washed in the solution of KI.

When sufficient iodide solution has been introduced into the bottle, it is agitated to ensure the absorption of the bromine and hydrobromic acid by the aqueous solution. The iodine now present is titrated with $\frac{N}{10}$ thiosulphate, and when the titration is completed 5 c.c. of a neutral 2 per cent solution of KIO_3 is added. This liberates a quantity of iodine corresponding to the hydrobromic acid formed, and on titrating this iodine the bromine substitution figure can be calculated.

The solution of KIO_3 should be tested for acidity by add-

ing a measured quantity to a solution of KI, and, if any iodine is liberated, it should be determined with thiosulphate and a suitable correction introduced into the calculation.

The reaction between bromine and oil appears to be practically instantaneous as far as the addition process is concerned; probably substitution is distinctly affected by the length of the determination.

1. The standard solution of bromine does not change on keeping. It is easily prepared.

2. The operation is quickly performed.

3. The absorption of bromine by addition is determined separately from the absorption by substitution, and thus additional information is gained.

4. The process is cheaper than that of Hübl. The CCl_4 is easily recovered.

Iodine Values of Typical Oils, Fats, and Waxes.

[Lewkowitsch.]

Drying Oils.	
Linseed	173–201
Candle-nut	163·7
Cedar-nut	159·2
Hemp seed	148
Linaria	140
Poppy seed	133–143
Asparagus seed	138
Henbane	131–138
Millet seed	130·4
Sunflower	119–135
Pine-nut	101·3
Tobacco seed	118·6
Semi-Drying Oils.	
Grape seed	96–143
Maize	111–130
Wheat	115·4
Cotton seed	108–110
Sesamé	103–108
Brazil-nut	106·2
Coumon	80
Rape (colza)	94–102
Black mustard	96–110
Non-Drying Oils.	
Almond	93–97
Acorn	100·7
Arachis	83–100
Rice	91·7–106·5
Sasanqua	82·0
Olive	79–88
Lycopodium	81
Castor	83–90
Animal Oils.	
Sardine	161–193
Salmon	161·42
Cod-liver	154·5–181·3
Shark-liver	114·6
Seal blubber	127–193
Neat's foot	69·3–76
Egg	68·5–81·6
Vegetable Fats.	
Nux vomica	69·4–79·3
Palm	51·5–57
Nutmeg butter	36–58
Cacao-butter	32–41
Borneo tallow	30

Palm-nut	13–17
Cocoa-nut	8–10
Japan wax	4·9–15·1
Animal Fats.	
Beef tallow	38–46
Mutton tallow	35–46
Lard	46–70
Butter	26–50

Waxes.	
Sperm oil	81–90
Flax wax	9·6
Wool wax	17·1–28·9
Bees-wax	7·9–11
Spermaceti	3·8
Insect wax	1·4

II.—The Acid Number.

The acid number is the number of milligrams of KOH required for the neutralization of the free acids in 1 gm. of sample.

Dissolve 1-2 gms. of the oil in 15-20 c.c. of ether-alcohol (2 : 1). Titrate the solution with $\frac{N}{10}$ potash (alcoholic) in the presence of phenolphthalein. Solid fats are dissolved in alcohol on the water bath and titrated warm.

III.—The Saponification Value (Köttstorfer).

Heat 1—2 gms. sample with 25 c.c. $\frac{N}{2}$ (approx.) alcoholic potash in a reflux apparatus on the water bath for half an hour.

Dilute with 20 c.c. water and titrate the excess of potash with $\frac{N}{2}$ acid.

Standardize the alcoholic potash by heating 25 c.c. under similar conditions without the addition of the oil and titrating with $\frac{N}{2}$ HCl.

The number of milligrams of KOH required for 1 gm. of oil is calculated. This value is the saponification value.

Saponification Value :—

Ester.	Products of Saponification of 100 Parts. Acid.	Glycerol.
Tributyrin	87·44	30·46
Trivalerin	88·96	26·77
Tripalmitin	95·28	11·41
Tristearin	95·73	10·34
Triolein	95·70	10·40

Saponification Number :—

Ester.	M.W.	Saponification Number.
Butyrin	302	557·3
Palmitin	806	208·8
Stearin	890	189·1
Olein	884	190·4

The saponification number is inversely proportional to the molecular weight of the acid combined with the glycerol.

IV.—The Acetyl Value.

$$R.OH + (CH_3CO)_2O = R.OCOCH_3 + CH_3.CO_2H$$
$$R.OCOCH_3 + KOH = R.OH + CH_3CO_2K.$$

The "acetyl value" is the number of milligrams of potash required by the acetyl derivative obtained from 1 gm. of oil.

Method due to Lewkowitsch.

Preparation of Alcoholic Potash.—Dissolve 32 gms. of 90 per cent stick potash in the least possible quantity of water and dilute to 1 litre with 96 per cent alcohol. Filter after standing for a day.

Ten gms. of the oil are boiled in a reflux apparatus for 2 hours with 20 gms. of acetic anhydride. The mixture is then poured into a litre flask and boiled for half an hour with 500-600 c.c. water, a slow stream of CO_2 being passed into the liquid to prevent bumping. After cooling, the upper aqueous layer is syphoned off and the lower oily layer is again boiled with water as above. This process is repeated three times.

The oil is finally filtered and washed with hot water on the filter paper until the filtrate is no longer acid. It is now dried in an oven and weighed.

Saponify 5 gms. of this acetyl compound with alcoholic potash. Evaporate off the alcohol and dissolve the residue in water.

Add dilute sulphuric acid (1 : 10) in excess and steam-distil the solution until 600-700 c.c. water have passed over.

The acidity of the filtrate is now determined with $\frac{N}{10}$ KOH solution with phenolphthalein as indicator.

The *Acetyl Value* is number c.c. $\frac{N}{10}$ KOH solution × 5·61 and divided by weight of oil.

Acetyl Values of Some Oils, Fats, and Waxes.

[Lewkowitsch.]

Linseed	3·98	Cocoa-nut	0·9–12·3
Rape	14·7	Lard	2·6
Olive	10·64	Beef tallow	2·7–8·6
Cod-liver	4·8	Butter	1·9–8·6
Seal	16·5	Wool wax	23·3
Palm	18·0	Bees wax	15·24
Cacao-butter	2·8	Spermaceti	2·63
Palm-nut	1·9–8·4		

V.—The Reichert-Meissl Value.

The Reichert-Meissl value is the number of c.c. $\frac{N}{10}$ alkali required for the neutralization of the volatile acids liberated from 5 gms. of oil by the Reichert distillation.

Five gms. of the oil sample are weighed into a 200 c.c. flask and saponified with alcoholic potash (2 gms. stick KOH in 50 c.c. 70 per cent alcohol). The residue, after evaporation of the alcohol, is dissolved in 100 c.c. water and 40 c.c. dilute sulphuric acid (1 : 10) are added.

Add a few pieces of pumice to the contents of the flask, and distil the liquid so that 110 c.c. pass over in one hour. Filter the distillate and titrate 100 c.c. with $\frac{N}{10}$ KOH solution with phenolphthalein as indicator.

Reichert-Meissl Values of Some Oils.

[Lewkowitsch.]

White acacia oil	1·2	Butter fat[1]	26–33[1]
Myrtle seed	9·65	Palm oil	5–6·8
Lycopodium	7·3	Linseed oil	0·0
Turtle	4·6	Olive oil	0·6
Macassar	9·0	Tallow	0·5
Cocoa-nut	7·0		

Saponification.

Modification for Discoloured Fats.—Parker C. McIlhiney ["J. Amer. Chem. Soc.," 16, 408 (1894)]. Two gms. of the fat are placed in an Erlenmeyer flask with a known excess of standard alcoholic NaOH. The alcohol is distilled off and 250 c.c. of 93 per cent alcohol added and heated till the soap dissolves. CO_2 is now passed into the solution for 1 hour to precipitate carbonate, then the solution is filtered into a large flask to which a spiral of platinum wire is added, and the alcohol distilled off. When most of the alcohol has evaporated 10 gms. NH_4Cl in 100 c.c. water are added and the ammonia distilled into an excess N . HCl (Fig. 16), and back titrated with N alkali using methyl orange as indicator.

One hundred c.c. of 93 per cent alcohol dissolves an amount of carbonate equivalent to 0·34 c.c. N acid, so that in calculating the result an allowance must be made to this extent, or of course a blank may be done side by side with the original experiment.

[1] (lowered by adulteration).

ALKALOIDS.

It is not proposed to deal with this specialized branch in any great detail, so that this survey is confined to the three most important general methods in use for this class of compounds, viz., the titration, the iodine and the polarimetric methods.

The Titration Method.—Alkaloids, being bases, combine with acid forming salts, so that by dissolving the base in excess of standard acid and titrating the excess of acid with standard alkali, using a suitable indicator, it is readily possible to calculate the amount of base present, provided the basicity is known.

This simple method is, however, beset by one great difficulty. It is absolutely necessary for success that the right indicator be chosen according to the alkaloid under examination.

Kippenberger ("Zeit. anal. Chem.," 1900, **39**, 201) has examined a whole series of alkaloids using different indicators, in order to compare their suitability. In general about 0·1 gm. of the alkaloid was dissolved in 50 c.c. $\frac{N}{50}$ H_2SO_4 in the presence of an aqueous solution of the indicator, and the excess of acid titrated against $\frac{N}{50}$ NaOH.

The following table gives a list of the commoner alkaloids, together with the most suitable indicators to employ in the several cases. Those in italics are preferable in use to the others:—

Aconitine—*Azolitmin*, iodeosin, hæmatoxylin, cochineal.
Atropine—*Lacmoid*, *uranine*, iodeosin, azolitmin, hæmatoxylin, cochineal.
Brucine—*Cochineal*, iodeosin, hæmatoxylin, azolitmin.
Cocaine—*Lacmoid*, uranine, cochineal, hæmatoxylin.
Codeine—*Iodeosin*, *lacmoid*, uranine, hæmatoxylin, cochineal.
Coniine—*Iodeosin*, *cochineal*, lacmoid, congo red.
Morphine—*Lacmoid*, *uranine*, iodeosin, azolitmin, hæmatoxylin, cochineal.
Narcotine—*Lacmoid* (methyl orange).
Nicotine—*Lacmoid* (iodeosin, uranine, cochineal).
Papaverine—*Lacmoid*.

Pelletierine—*Cochineal*, uranine.
Quinine—*Azolitmin*, *hæmatoxylin*, uranine, lacmoid + ether.
Strychnine—*Azolitmin*, iodeosin, hæmatoxylin, cochineal.
Thebaïne—*Iodeosin*, *cochineal*, uranine (lacmoid).
Veratrine—*Lacmoid*, iodeosin, hæmatoxylin, cochineal.

The majority of these indicators are well known. Uranine is synonymous with fluorescein ; iodeosin is tetraiodofluorescein and hæmatoxylin is the extract from logwood. The remainder call for no comment.

In all cases, except iodeosin, the indicator was in aqueous solution. Iodeosin was in ether solution added to the aqueous liquid and the whole well shaken after every addition of alkali.

Messner [" Zeit. angew. Chem.," 1903, 16, 444] has investigated the application of various indicators to the quinine group. From his results he condemns the use of azolitmin, cochineal, congo red and methyl orange for these alkaloids. Hæmatoxylin gives untrustworthy results except in the hands of experienced workers. Lacmoid in ether solution gives good results provided the solution be vigorously shaken during the titration. Iodeosin is much more reliable in ether-alcohol solution than in ether alone. He considers that the most reliable indicator for this class is an alcoholic solution of lacmoid. Commercial lacmoid must be purified by extraction with ether which is afterwards evaporated off on the water bath. For use 0·2 gm. lacmoid is dissolved in 100 c.c. 90 per cent alcohol.

Twenty c.c. of an $\frac{N}{20}$ alcoholic quinine solution are diluted with 40 c.c. alcohol and one to two drops of the indicator solution added. $\frac{N}{10}$ HCl is run in without shaking till the colour changes sharply from blue to red.

This indicator, used in this way, allows of the accurate titration of the weak quinine bases with such weak acids as acetic and tannic acids. Excellent results were obtained with quinine and quinidine, cinchonine, and cinchonidine.

The Iodine Method.—Christensen ["Chem. Zeit.," 1890, p. 1346].

A known quantity of the alkaloid is dissolved in an excess of $\frac{N}{10}$ H_2SO_4 and dilute alcohol, made up to 50 c.c. with water, and 50 c.c. of ordinary alcohol added. To this mixture is added an excess of KI solution (1 : 15) and KIO_3 solution (1 : 25) whereby the amount of H_2SO_4, over that required for the formation of the sulphate, is determined from the iodine which it sets free according to the equation :—

$$3H_2SO_4 + 5KI + KIO_3 = K_2SO_4 + 3H_2O + 6I$$

The iodine is titrated against standard thiosulphate until the yellow colour just vanishes.

If A = number of c.c. of $\frac{N}{10}$ H_2SO_4 added

a = number of c.c. of $\frac{N}{10}$ thiosulphate required.

V = equivalent number of the base.

then the weight of alkaloid = $\frac{V\,(A - a)}{10{,}000}$.

All plant alkaloids except pilocarpine, narcotine, and theobromine can be estimated by the above method.

The Polarimetric Method.—Hesse ["Annalen," 1876, 182, 146]; Oudemans ["Annalen," 1876, 182, 63].

As most alkaloids are optically active they can be estimated in the polarimeter in exactly the same manner as the sugars, q.v.

$$\left[a\right] = \frac{100\,a}{lc}$$

where a = angle of rotation observed.

l = length of the polarizing tube in decimetres.

c = number of gms. of substance in 100 c.c. of solution.

A mixture of two alkaloids is easily estimated in this way. One gm. of a mixture of two alkaloids A and B (50 per cent each) was dissolved in 25 c.c. of 97 per cent alcohol

and put into a 2-decimetre tube. The angle of rotation was + 3·48° giving $[a]_D = 43·5°$.

The specific rotation of pure A in approximately the same concentration (4 per cent) was − 142·57°, and of pure B + 224·74°.

If x = weight of A in 1 gm. mixture.
y = weight of B in 1 gm. mixture.

$$x + y = 1$$
$$-142·57\,x + 224·74\,y = 43·5$$

whence $x = 0·491$ instead of 0·5
$y = 0·509$ „ 0·5.

By making use of the alteration of the specific rotation with the solvent used, a mixture of three alkaloids can be determined.

A mixture of cinchonine, cinchonidine, and quinidine was made containing per gm.

Cinchonine	0·0562 gm.
Cinchonidine	0·5151 „
Quinidine	0·4287 „
	1·0000 „

Two gms. of the mixture were dissolved in 100 c.c. 97 per cent alcohol and 25 c.c. put into a 2-decimetre tube. The observed angle of rotation was 2·78° giving $[a]_D = 69·5$.

A 2 per cent solution in HCl (3 molecules HCl to 1 of alkaloid) was then used in the 2-decimetre tube, and the angle of rotation was 2·82° giving $[a]_D = 64·09$.

Pure Substances.	Specific Rotations of 2 per cent Solutions in 97 per cent Alcohol.	HCl Solution.
Cinchonine	226·13	259·12
Cinchonidine	−106·89	−177·47
Quinidine	261·77	329·94

If x = weight of cinchonine per gm. of mixture.
y = „ cinchonidine „ „
z = „ quinidine „ „

$$x + y + z = 1.$$

$$226{\cdot}13\,x - 106{\cdot}89\,y + 261{\cdot}77\,z = 69{\cdot}50$$

$$259{\cdot}12\,x - 177{\cdot}47\,y + 329{\cdot}94\,z = 64{\cdot}09$$

whence $x = 0{\cdot}1036$ instead of $0{\cdot}0562$

$y = 0{\cdot}5135$,, $0{\cdot}5151$

$z = 0{\cdot}3829$,, $0{\cdot}4287$

ALCOHOLS.

Estimation of Methyl Alcohol.

The methods described for the estimation of alcohol are of a varied character, but none is accurate.

1. Oxidation with dichromate :—
   (*a*) by measuring CO_2 evolved,
   (*b*) by titrating excess of dichromate.
2. Conversion to methyl iodide which is measured.
3. Application of Zeisel's reaction.
4. Formation of definite compounds.

I.—(*a*) Method of Thorpe and Holmes.

(*b*) (i) Method of O. Hehner. In this, the excess of dichromate is estimated by a solution of ferrous sulphate.

(ii) Method of O. Blank and H. Finkenbeiner. The excess of chromic acid is estimated by the titration of iodine liberated on the addition of potassium iodide.

II.—Methods in this class are those of F. Fischer, and A. Lam.

III.—Methods of Stritar and Zeidler, and Stritar.

IV.—Method of Vyvere.

I.—(*a*) Method of T. E. Thorpe and J. Holmes ["Trans. C. Soc.," 1904, 85, 1].

Methyl Alcohol in Presence of Ethyl Alcohol.

The sample is mixed with water in such proportion that 50 c.c. of the mixture shall contain not more than 4 gms. of the mixed alcohols.

Fifty c.c. of this mixture are introduced into the oxidation flask, 300 c.c. (Fig. 47), provided with a ground-in stopper, and fitted with a funnel and side tube. To this 20 gms. of potassium dichromate and 80 c.c. of dilute sulphuric acid (1 : 4) are added, and the mixture allowed to remain for 18 hours. A further quantity of 10 gms. of potassium dichromate

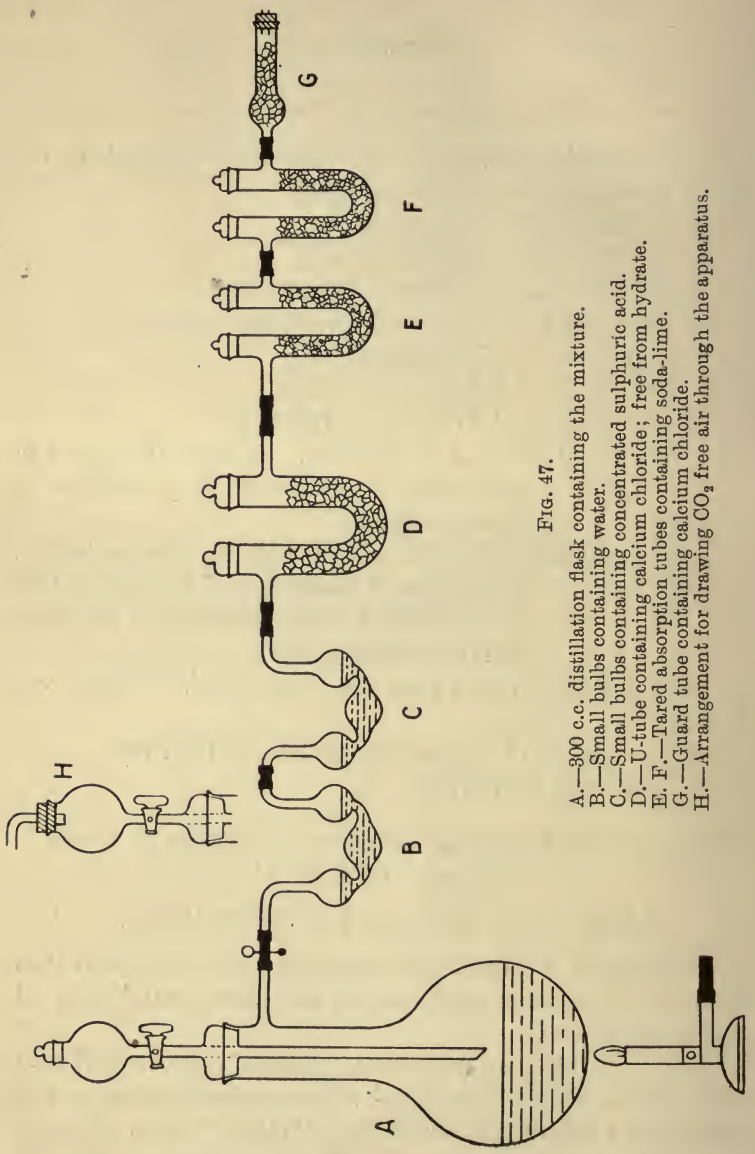


FIG. 47.

A.—300 c.c. distillation flask containing the mixture.
B.—Small bulbs containing water.
C.—Small bulbs containing concentrated sulphuric acid.
D.—U-tube containing calcium chloride; free from hydrate.
E. F.—Tared absorption tubes containing soda-lime.
G.—Guard tube containing calcium chloride.
H.—Arrangement for drawing CO_2 free air through the apparatus.

and 50 c.c. of sulphuric acid mixed with an equal volume of water are now added, and the contents of the flask heated to boiling-point for 10 minutes, the evolved carbon-dioxide being swept out of the apparatus by a current of air and collected in weighed soda-lime tubes.

Under the conditions of oxidation, a quantity not exceeding 0·5 per cent of ethyl alcohol is transformed into carbon dioxide, the remainder being converted into acetic acid.

Methyl alcohol is wholly decomposed into carbon dioxide and water.

When ethyl alcohol is present, a subtractive correction must be applied to the weight of carbon dioxide thus obtained, in the proportion of 0·01 gm. of carbon dioxide for each gm. of ethyl alcohol present.

The aggregate quantity of the two alcohols present can be found approximately from a table of densities.

Let x = amount methyl alcohol.
y = amount ethyl alcohol.
a = total amount by density.
b = weight CO_2

Then $x + y = a$.

$$\frac{44}{32}x + \frac{0{\cdot}5}{100} \times \frac{44}{60}y = b$$

whence x and y can be calculated.

(*b*) (i) Method of O. Hehner [" Analyst," 12, 25].

Since 1 part of ethyl alcohol reduces 4·278 parts of potassium dichromate whilst one part of methyl alcohol requires 9·224 parts, the proportion of the two can be deduced by the amount of dichromate required to oxidize a mixture of the alcohols.

Dichromate solution :—

Eighty gms. $K_2Cr_2O_7$, 150 c.c. concentrated sulphuric acid in 1 litre.

About 0·2 gm. alcoholic mixture is diluted and mixed with 25-30 c.c. of the dichromate solution, which is corked up in a pressure flask and heated in boiling water for 2 hours.

The unreduced dichromate is then estimated by iron solution and standard dichromate solution.

(ii) Method of Oskar Blank and H. Finkenbeiner ["Ber.," 1906, 39, 1326].

Estimation of Methyl Alcohol in Solutions of Formaldehyde.

The authors describe a method of determining methyl alcohol in commercial formaldehyde, which generally contains from 12 to 18 per cent of methyl alcohol. A weighed amount of the formaldehyde solution is added to a solution of standard chromic acid to which sulphuric acid has been added. After 12 hours at the ordinary temperature the solution is diluted; to an aliquot portion potassium iodide is added and the solution then titrated with standard thiosulphate solution.

II.—(*a*) Method of A. Lam. ["Zeit. angw. Chem.," 1898, 125].

25 c.c. of the spirit, the sp. gr. of which should be about 0·935, is treated with 5 gms. amorphous phosphorus and 40 gms. of iodine in a distilling flask. When the action is over the contents are distilled, and the iodides are first washed with weak aqueous soda, then with water, and are then dried over calcium chloride.

After noting the volume the sp. gr. is carefully taken, and the amount of methyl iodide ascertained by referring to the tables given in the original paper.

The sp. gr. methyl iodide is 1·9444 and that of ethyl iodide is 2·2677.

(*b*) Method of F. Fischer ["Dingl. Polyt. J.," 215, 82].

Estimation of Methyl Alcohol. In Commercial Wood Spirit.

The apparatus used for this method consists of a fractional distillation flask 30-40 c.c. in capacity, with long neck and T-branch, proceeding at right angles, of considerable length.

It is connected to a Liebig condenser to the end of which is fixed an adaptor dipping into a measuring tube graduated to 0·1 c.c.

The flask is fitted with a thermometer through a rubber stopper.

Five c.c. wood spirit are introduced into the apparatus with sufficient phosphorus iodide (30 gms.) and the mixture heated with the apparatus inclined so that it acts as a reflux.

On termination of the action, the methyl iodide is distilled off, the final traces of iodide being removed by a stream of carbon dioxide.

Phosphorus iodide.—15·5 gms. phosphorus are dissolved in 350 c.c. of carbon disulphide, 127 gms. iodine are added and the whole is cooled.

The crystals are dried in air.

III.—(*a*) Method of Milan J. Stritar ["Zeit. anal. Chem.," 1904, 43, 401].

Estimation of Methyl Alcohol in Commercial Formaldehyde.

Commercial formalin is diluted with twenty volumes of water and treated with an excess of ammonia. The mixture is distilled until about one half is passed over. The distillate, which contains formaldehyde in traces only, is feebly acidified with acetic acid and a convenient portion is submitted to Zeisel's iodide process.

(*b*) Method of Milan J. Stritar and H. Zeidler ["Zeit. anal. Chem.," 1904, 43, 387].

Methyl Alcohol in the Products of Distillation of Wood.

Substances interfering with Zeisel's iodide method for methyl alcohol are allyl alcohol, methyl acetate, methylal, acetaldehyde, formaldehyde, acetone, guaiacol, creosol, and the dimethyl esters of pyrogallol and its homologues.

Allyl iodide yields *iso*propyl iodide and the corresponding amount of silver iodide. It must be determined by the bromine addition method and allowance made for it. The amount of

formaldehyde is insignificant, and the rate of formation of methyl iodide is very slow compared with methyl alcohol. Acetaldehyde and acetone yield no volatile iodide. Methylal yields two molecules of silver iodide, but no method of correction is known.

Methyl acetate also yields silver iodide corresponding with its methoxyl group. A correction may be obtained from the esterification value of the wood spirit by estimating the ester value. Guaiacol and the other phenolic ethers are eliminated by means of animal charcoal. The latter absorbs some methyl alcohol which is recovered by a slight washing.

(*a*) Five c.c. crude spirit are diluted to 500 c.c., and 5 c.c. are submitted to the iodide process. The weight of silver iodide multiplied by 272·94 gives grammes of methyl alcohol per 100 c.c.

(*b*) Aqueous wood spirit containing less than 10 per cent methyl alcohol is diluted to five times its volume (10 c.c. to 50 c.c.), shaken for a quarter of an hour with 0·5 gm. animal charcoal filtered through a small moistened filter, the charcoal washed slightly and the filtrate is made up to 100 c.c. Five c.c. are submitted to the iodide process.

(*c*) Of crude pyroligneous acid, 50 c.c. are neutralized with sodium carbonate, made up to 250 c.c. and filtered through an unmoistened filter paper; 100 c.c. are then made strongly alkaline with sodium hydroxide and distilled until 50 c.c. have been collected.

Dilute aqueous solutions of methyl alcohol can be distilled without loss. The distillate is treated with charcoal, as above, and 5 c.c. used for the Zeisel's process (see Chap. III).

IV.—Method of Van de Vyvere [" Chem. Centr.," 1884, 69].

Estimation of Methyl Alcohol in Ethyl Alcohol.

Methyl alcohol forms a compound with calcium chloride which is not decomposed by heat at 100°, but is decomposed by water.

The sample is distilled over anhydrous sodium carbonate on a water bath and the volume of distillate is measured.

An aliquot part of the distillate is allowed to remain over an equal weight of anhydrous calcium chloride for twenty-four hours. The ethyl alcohol is then distilled off; the residue, when treated with water, yields a mixture of alcohol and water on distillation. From tables the amount of alcohol present may be calculated.

Estimation of Ethyl Alcohol.

Amongst the many methods which have been suggested for the determination of this alcohol, the following have been chosen as illustrations:—

1. Physical methods—
   (*a*) E. Duclaux.
   (*b*) E. Maumené.
2. Colour reaction—G. Argenson.
3. Oxidation method—
   (*a*) By permanganate—B. Röse.
   (*b*) By dichromate—Benedict and Norris. Thorpe and Holmes (see methyl alcohol).
4. Conversion to alkyl iodide and estimation as silver salt—L. Prunier.

I.—(*a*) Method of E. Duclaux ["Ann. Chim. Phys." (5) II., 233].

This method depends upon the surface tension of alcohol and of aqueous solutions.

Various tables for use in this connexion are to be consulted in the original paper.

(*b*) Method of E. Maumené ["Compt. rend.," 83, 67].

The author modifies Gay Lussac's method of estimating alcohol as follows:—

Two hundred c.c. of sample containing not more than 15 per cent of alcohol are distilled to one half measure at 15° C. and rendered slightly alkaline with caustic soda. The alcohol in the distillate at 15° is determined by means of a centigrade alcoholometer, the degrees of which are referred to a special table contained in the original paper.

If the distillate contains ammonia, this is neutralized with a few drops of sulphuric acid.

For other physical methods of estimation, consult the article on "Alcoholimetry" in the "Dictionary of Applied Chemistry," vol I, T. E. Thorpe.

II.—Method of G. Argenson ["Bull. Soc. Chim.," 1902, 27, III, 1000].

Alcohol in Dilute Solutions.

A 0·05 per cent solution of magenta decolorized to a faint pink with SO_2, and a saturated solution of potassium dichromate are required.

Add 5 c.c. dichromate solution and 1 c.c. of sulphuric acid to 20 c.c. alcoholic liquid containing from $\frac{1}{100000}$ to $\frac{1}{200000}$ of its volume of alcohol. This mixture is distilled, and the first 5 c.c. collected in a test glass containing 5 c.c. magenta solution.

This tint is matched against the distillate from a liquid containing a known quantity of alcohol which is used to standardize a solution of potassium permanganate.

III.—(*a*) Method of B. Röse ["Zeit. angew. Chem," 1, 31].

About 5 gms. of dilute alcohol (1 per cent) is weighed into a flask; 50 c.c. of permanganate solution (10 gms. of $KMnO_4$ in a litre) is run in, and then 20 c.c. sulphuric acid whilst shaking. After a few minutes 100 c.c. water is added, then a measured excess of standard oxalate solution, the liquid heated nearly to boiling, and excess of oxalate found by titration against permanganate. In four experiments 100·18, 100·0, 100·24, and 100·0 per cent of the alcohol present was indicated.

This method has been criticized by L. Grünhut ["Chem. Zeit.," 15, 847]. He says that a good deal depends on the amount of strong sulphuric acid added; if added in insufficient quantity, a very incomplete oxidation occurs. If, on the other hand, too much acid is added an independent decomposition of the permanganate sets in.

(*b*) Method of F. G. Benedict and R. S. Norris ["J. Amer. Chem. Soc.," 1898, 20, 293].

Twenty c.c. of chromic acid solution (dissolve 2·2064 gms. $K_2Cr_2O_7$ in little water, make up to 500 c.c. with concentrated H_2SO_4 below 100° C.) are delivered from a burette into a flask containing 200 c.c. water and ferrous sulphate solution is added from a burette until the chromate is reduced, any excess being titrated with equivalent permanganate.

Twenty c.c. of the chromic acid solution are now mixed in a small flask with 5 c.c. alcohol (2 gms. of exactly 5 per cent alcohol mixed with 5 c.c. sulphuric acid at low temperature and diluted to 50 c.c.) and heated for 5 minutes to 98° which temperature must not be exceeded. When cold, dilute with 200 c.c. water and titrate with iron solution.

The difference in c.c. between the amounts of ferrous ammonium sulphate solution used to reduce the two amounts of chromic acid solution will represent the amount of alcohol present.

Unknown solutions of alcohol are first tested as to approximate strength by density, and then sufficient is taken to correspond with the amount used in the check experiment.

IV.—Method of L. Prunier ["J. Pharm.," (5), 29, 407].

Separation and Estimation of Small Quantities of Methyl and Ethyl Alcohols.

The alcoholic liquid is treated with concentrated hydriodic acid to convert the alcohols into the corresponding halogen compounds, and then shaken with pure chloroform, or distilled and the first portions condensed in a receiver containing chloroform.

After removing free acid by shaking with aqueous potash the chloroform is agitated with a solution of silver nitrate and a little moist silver oxide which will produce a precipitate of silver iodide. This is washed, first with ammonia and then with nitric acid, and weighed.

If ethyl alcohol alone is present, its amount may be at once calculated from the weight of the silver iodide ; if both alcohols are present their total amount must be ascertained from the density of the distillate, and their respective amounts calculated from the amount of silver iodide obtained.

Glycerol.

The methods in general use are :—

1. Bichromate Method, in which the glycerol is oxidized by $K_2Cr_2O_7$, and H_2SO_4 to CO_2 (Hehner, Richardson, and Jaffé).

2. Acetyl Estimation, whereby the triacetyl compound is formed and estimated by hydrolysis (Benedict and Cantor).

3. Iodine Method.—Glycerol treated with HI gives *iso*propyl iodide, which is decomposed with $AgNO_3$ and the silver iodide weighed (Zeisel and Fanto).

1. (*a*) Hehner's Method.

["J. Soc. Chem. Ind.," 1889, 8, 5].

The solutions required are :—

(i) Bichromate solution: 74·86 gms. per litre and 150 c.c. concentrated H_2SO_4. The exact strength is got by standardizing against pure iron or ferrous ammonium sulphate.

(ii) Ferrous ammonium sulphate solution : 240 gms. per litre.

(iii) Bichromate solution : one-tenth the strength of (i). The ferrous ammonium sulphate solution is exactly standardized on this, and the glycerine value of (i) calculated by dividing the content of bichromate by 7·486.

Estimation of Crude Glycerine.—About 1·5 gms. of the sample are weighed out into a 100 c.c. flask and Ag_2O added to remove chlorides and aldehydes. A little water is added and the flask left to stand for 10 minutes when it is treated with a slight excess of basic lead acetate and made up to mark. Twenty-five c.c. are removed and filtered into a perfectly clean beaker, 40-50 c.c. of the standard bichromate solution (i) added, together with 15 c.c. concentrated H_2SO_4. The beaker is covered with a watch glass and heated for 2 hours on the water bath. The excess of $K_2Cr_2O_7$ is then titrated against the ferrous ammonium sulphate solution.

$$3C_3H_8O_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 7K_2SO_4 + 7Cr_2(SO_4)_3 + 40\ H_2O + 9CO_2.$$

Glycerine in Soaps and Fats.—Three gms. are saponified by alcoholic KOH, retaining the alcohol, and the solution diluted to 200 c.c. A little H_2SO_4 is added and the insoluble acids filtered off. The filtrate and washings—about 500 c.c. —are boiled vigorously down to 250 c.c. in a covered beaker, then H_2SO_4 and $K_2Cr_2O_7$ added as before.

(*b*) Modification of Hehner's Method.

Richardson and Jaffé ["J. Soc. Chem. Ind.," 1898, 17, 330].

Twenty-eight gms. of the sample of crude glycerine are made up to 50 c.c. with ordinary water and 25 c.c. treated with 7 c.c. of basic lead acetate solution. The precipitate is filtered off into a 250 c.c. flask and washed with about 150 c.c. cold water. The small excess of lead is precipitated by dilute H_2SO_4, the liquid made up to the mark, and the whole well shaken up. Twenty-five c.c. (= 2 gms. original sample) are filtered into a beaker, the mouth of which is closed by a funnel with short stem, 25 c.c. Hehner's $K_2Cr_2O_7$ solution, and finally 25 c.c. pure H_2SO_4 are cautiously mixed with the other liquid, and the whole heated on the water bath for 20 minutes, when the oxidation is complete. Then the mixture is cooled, made up to 250 c.c., and 20 c.c. portions titrated against ferrous ammonium sulphate solution (2·982 per cent), using potassium ferricyanide as external indicator.

The portion of iron solution taken represents 0·01 gm. glycerine. If A = number of c.c. bichromate solution required

x = per cent glycerine,

$$\text{then } x = (0{\cdot}25 - \frac{250}{A} \times 0{\cdot}01) \times 500.$$

0·25 is the equivalent of glycerine represented by the 25 c.c. bichromate used containing 74·86 gms. per litre.

In the case of spent lye 2·5 gms. are taken and a slight excess of basic lead acetate added to precipitate chlorides and organic matter. The procedure is then as above except that the $PbSO_4$ is filtered off and the filtrate concentrated to 25 c.c. before addition of $K_2Cr_2O_7$ and H_2SO_4.

The treatment with Ag_2O is considered unnecessary.

2. The Acetyl Method.

Benedict and Cantor ["Monats.," 9, 521].

1·5 gms. of crude glycerine are heated to the boiling-point with 7 gms. acetic anhydride and 3 to 4 gms. of anhydrous sodium acetate (freshly heated before use) under a reflux for 1½ hours. The liquid is cooled, 50 c.c. water added, and reheated below the boiling-point to dissolve the triacetyl compound. The contents of the flask are filtered, the residue washed, and the filtrate exactly neutralized with a 2-3 per cent solution of NaOH, a little phenolphthalein being used as indicator. Twenty-five c.c. of a 10 per cent standard NaOH solution are added, and the whole boiled to complete the hydrolysis. The excess of KOH is titrated against standard acid.

1 c.c. N acid ≡ 0·03067 gms. glycerol.

It is necessary to conduct the operations as quickly as possible since the triacetyl derivative is somewhat hydrolyzed by water.

3. Iodine Method.

Zeisel and Fanto [through "Chem. Ztg. Rep.," 1902, 173].

The decomposition is effected in the small flask *a*, 40 c.c., (Fig. 48) provided with a CO_2 inlet. As much of the substance as will give about 0·4 gm. AgI, together with 15 c.c. of aqueous HI (sp. gr. 1·9), are introduced into *a* and heated on a glycerine bath. The condenser *b* is coupled to Ehmann's warming apparatus *g* kept full of water at 50-70° C. As in methoxyl determinations a wash flask, containing a suspension of red phosphorus, is provided. The conical flasks *e* and *f* containing respectively 45 c.c. and 5 c.c. of a 4 per cent. alcoholic solution of $AgNO_3$. The CO_2 is driven through at about three bubbles per second.

At the end of the distillation the contents of *e* and *f* are rinsed out, diluted to 450 c.c., mixed with 10-15 c.c. dilute

$AgNO_3$, heated on water bath, cooled, and the AgI estimated either gravimetrically or volumetrically.

If gravimetrically, weight AgI × 0·3922 = weight of glycerol.

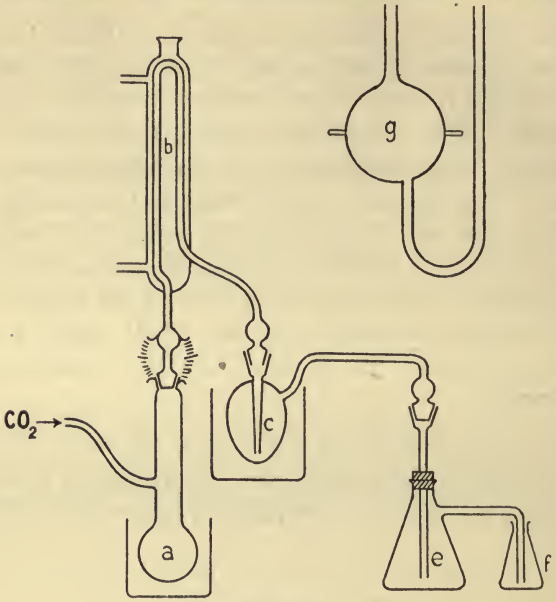


Fig. 48.

Notes on the Above Methods.

Schulze ["Chem. Ztg.," 1905, 29, 976], has submitted all the general methods to strict comparative tests. He finds that Hehner's methods gives results $\frac{11}{10}$ of the correct, so that he takes 74·86 gms. $K_2Cr_2O_7 \equiv 11$ gms. glycerine instead of 10 gms.; further, the presence of phosphoric acid renders the method useless. The acetyl determination is of little use for dilute solutions unless a large number of determinations are made and the mean taken. The iodine method is most accurate but it is too costly for technical use.

PHENOLS.

I.—Precipitation of Bromine Derivatives.

The earliest method under this heading is that suggested by Landolt ["Ber.," 4, 770] and consisted simply in the precipitation of phenol with bromine:—

$$C_6H_5 \cdot OH + 4Br_2 = C_6H_2Br_4O + 4HBr.$$

This method has undergone modifications suggested by Koppeschaar ["Zeit. anal. Chem.," 25, 162], Weinreb and Bondi ["Monats.," 6, 506], Kossler and Penny ["Hoppe Seyler's Zeit. physiol. Chem.," 17, 133], Toth ["Zeit. anal. Chem.," 25, 162].

Method of Koppeschaar.

This method originally consisted in adding to an aqueous solution of the phenol a solution of bromine in caustic soda in the presence of hydrochloric acid. After standing for some time the excess of bromine is estimated by the addition of potassium iodide and the liberated iodine titrated with thiosulphate solution.

$$C_6H_5OH + 4Br_2 = C_6H_2Br_4O + 4HBr.$$
$$C_6H_2Br_4O + 2KI = C_6H_2Br_3OK + KBr + I_2$$

It will be seen that each molecule of phenol will correspond to 6, and not 8 atoms of bromine as the original tetrabromophenol is partially decomposed by the potassium iodide.

This method has been modified in various smaller details. Giacosa ["Zeit. physiol. Chem.," 6, 45] adds bromine water to an aqueous solution of phenol until the supernatant liquid commences to turn iodized starch paper blue.

Chandelon ["Bull. Soc. Chim.," 38, 75] adds a dilute phenol solution to potassium hypobromite solution until the liquid no longer acts on iodized starch paper. See also Seubert ["Jahresberichte der Chem.," 1881, 1204].

II.—Precipitation of Iodine Derivatives.

Messinger and Vortmann ["Ber.," 22, 2313] have shown that when iodine dissolved in potassium iodide is added to a strongly alkaline solution of a phenol warmed to 50°-60° C., coloured iodine compounds are formed.

$$C_6H_5OH \rightarrow C_6H_3I_3O.$$

Messinger and Vortmann ["Ber.," 23, 2753] have devised a quantitative method for phenols on this basis.

Phenol.—Two to three gms. of phenol are dissolved in a solution of sodium hydrate free from nitrate, so that for 1 molecule of phenol there are 3 molecules of alkali present. The solution is diluted to 250-500 c.c. and a known volume (10 c.c.) is placed in a flask heated to 60°. A $\frac{N}{10}$ iodine solution is now run in until the liquid is yellow, showing excess of iodine. By shaking up, a red precipitate is produced. Cool and acidify with dilute sulphuric acid; dilute to 250 or 500 c.c. Filter 100 c.c. and titrate with $\frac{N}{10}$ thiosulphate.

Wt. of iodine used × 0·123518 = wt. pure phenol.

$$\frac{1 \text{ molecule phenol}}{6 \text{ atoms iodine}} = 0{\cdot}123518.$$

Thymol.—0·1 to 0·3 gm. is dissolved in sodium hydrate solution so that 1 molecule of thymol is present with 4 molecules of NaOH.

The procedure is the same as described under phenol except that the action is completed in the cold.

1 molecule thymol requires 4 atoms iodine.

Factor = 0·29568.

β Naphthol.—Dissolve 0·1 to 0·3 gms. in sodium hydrate solution so that 1 molecule naphthol is present with 4 molecules of NaOH. A dirty green precipitate is produced; the procedure is the same as for the estimation of phenol.

1 molecule β naphthol requires 3 atoms of iodine.

Factor = 0·37843.

Salicylic Acid.—The acid can be here estimated in the presence of benzoic acid.

Proceed as described for phenol. A red precipitate is produced.

1 molecule salicylic acid requires 6 atoms of iodine.

Factor = 0·18133.

III.—Direct Titration with Alkalis.

Method of Bader ["Zeit. anal. Chem.," 31, 58].

Phenol is estimated by direct titration with normal caustic soda using tri-nitrobenzene as indicator. This method is not of general application as most phenols give highly coloured salt solutions.

A. W. Titherley ["Trans. C. Soc.," 1894, 66, 504] described the action of sodamide on phenols.

$$C_6H_5OH + NaNH_2 = NaOC_6H_5 + NH_3$$

This property was made use of by S. B. Schryver ["J. Soc. Chem. Ind.," 1899, 554].

The principle of the method consists in the treatment of phenol in a solution of a substance having no action on sodamide, and estimating the ammonia by volumetric methods.

Benzene was usually employed by the author.

The sodamide (1 gm.) is finely powdered, washed several times with benzene and then introduced into a 200 c.c. wide-mouthed flask (A) connected with a reflux condenser (Fig. 49).

About 50 or 60 c.c. of thiophene-free benzene are added and the mixture boiled on a water bath, while a current of air (dry and free from CO_2), drawn by means of an aspirator or pump through a separation funnel (B) which dips under the surface of the liquid, is continually drawn through the apparatus. The boiling is carried on for 10 minutes so as to remove all traces of ammonia which adhere to the sodamide.

About 20 c.c. of normal sulphuric acid are placed in the absorption bottle (C) and the phenol dissolved in about six times its weight of benzene is placed in the separating funnel.

This solution is allowed to drop slowly into the flask (A) which is kept in a constant state of ebullition and connected with the aspirator. The funnel is finally washed with benzene, and air drawn through until no more ammonia remains unabsorbed. This time is usually 1½ hours, as ammonia is held very strongly by the benzene.

Enough phenol is used to require from 10-17 c.c. N. sulphuric acid for the neutralization of the ammonia evolved.

The excess of acid is titrated with normal sodium carbonate, using methyl orange as indicator.

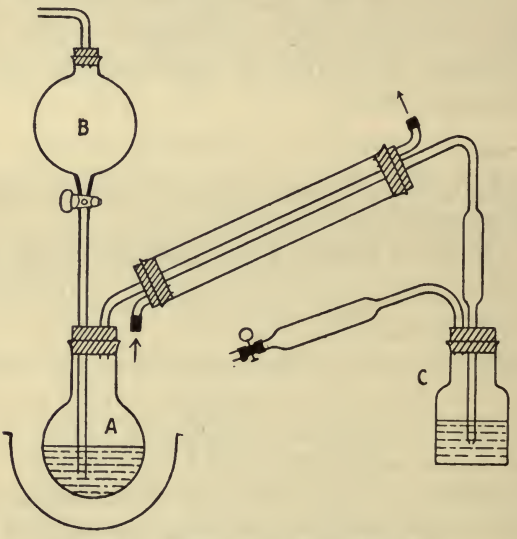


FIG. 49. (From Jour. Soc. Chem. Ind.)

N.B.—(1) The phenol and apparatus must be absolutely free from moisture.

(2) Sufficient benzene must be employed, as some salts are insoluble in this solvent and the tubes are likely to become clogged.

(3) Benzene must be free from thiophene, as sulphur compounds interfere with the delicacy of the indicator.

(4) Air should be aspirated for a sufficient length of time.

Xylene or toluene can be used but a sand bath is then necessary in place of a water bath.

Other methods of analysis are described in the following pages :—

Volumetric Estimation.

J. F. Tocher ["Pharm. J.," 1901 (iv), 12, 360].

A known volume of an aqueous solution of phenol is rendered alkaline by the addition of sodium hydrogen carbonate. To this mixture is added an excess of $\frac{N}{10}$ potassium permanganate solution and the liquid is boiled for five minutes. After cooling it is acidified with dilute sulphuric acid, warmed to 60°, and excess of permanganate titrated with $\frac{N}{10}$ oxalic acid solution.

$$C_6H_5OH + 7O_2 = 6CO_2 + 3H_2O.$$

1 c.c. $\frac{N}{10}$ permanganate $\equiv$ ·0003358 gm. phenol.

The following modification of Tocher's method was found to give good results :—

C. M. Pence ["Chem. News," 1913, 108, 74].

Dissolve 0·4 gm. phenol in a litre of water. Put 50 c.c. $\frac{N}{10}$ permanganate and 3-4 gms. $NaHCO_3$ in a 500 c.c. glass-stoppered Erlenmeyer flask. Add 25 c.c. of the phenol solution with gentle rotation. Boil 5-10 minutes with stopper removed. Cool flask to about 60° C. Acidify with dilute H_2SO_4, let stand about two minutes; cool to room temperature. Dilute with distilled water, add 5 c.c. 20 per cent KI solution and titrate the liberated iodine with $\frac{N}{10}$ thiosulphate, using starch.

The number of c.c. of $\frac{N}{10}$ thiosulphate subtracted from the number of c.c. $KMnO_4$ originally added = number c.c. of $KMnO_4$ consumed by the phenol.

1 c.c. $\frac{N}{10}$ $KMnO_4$ = 0·000336 gm. phenol.

If a glass-stoppered Erlenmeyer flask is not available, an ordinary Erlenmeyer may be used and its contents transferred to a glass-stoppered bottle before acidifying. Any oxide adhering to the flask may be removed by the addition of a little dilute H_2SO_4 containing a few drops of 20 per cent KI solution.

Method of T. Chandelot.

["Bull. Soc. Chim." (2) 38, 69].

Preparation of Hypobromite Solution.—Dissolve 14 to 15 gms. of pure potash in a litre of water and add gradually 10 gms. of bromine. This solution is standardized by means of a known solution of pure phenol. This latter solution is made by dissolving 5 gms. in a litre of water, so that 10 c.c. contain 0·05 gms. of phenol. The hypobromite solution, kept in a dark place, is diluted until 50 c.c. correspond to 10 c.c. of the phenol solution.

50 c.c. of the bromine solution are placed in a flask and the phenol solution, which must be dilute, is added until a drop of the solution gives no colour with iodized starch paper placed on a white porcelain tile.

The method is serviceable in clinical operations; the error may be about 1·2 per cent.

The strength of the phenol solution as a percentage is obtained directly by dividing the number of c.c. used into 5.

Let a = number c.c. phenol solution used.

then $a : 0{\cdot}05 = 100 : x$

whence $x = \frac{5}{a}$

Concentrated solutions (3 to 5 per cent) must be diluted one-tenth, as an error in reading of 0·1 c.c. may introduce an error of 17 per cent in the estimation, whereas in the dilute solution the error may be 2 per cent.

Method of L. Zimmerman.

["J. Pharm." [5] 29, 105].

As a modification of Chandelot's method, the following is suggested by the author.

The strength of a hypobromite solution is found by titration against a phenol solution of known strength. The indicator used is iodized starch paper impregnated with sodium carbonate.

Owing to the lack of sensitiveness of the indicator, it is necessary to apply a correction if the dilution of phenol in water should be greater than 1 gm. in 250 c.c. This correction is proportional to the square of the dilution, $y = ax^2$, the value of a corresponding with 20 c.c. of Chandelot's hypobromite is 0·00434.

The original memoir contains tables from which the strength of the solution of phenol may be easily determined.

Mixture of Phenol and Cresols.

Hugo Ditz and Franz Cedivoda ["Zeit. angew. Chem.," 1899, 873, 897].

Impurities are removed from the phenolic mixture by extraction with ether, the ethereal extract being dried over anhydrous calcium chloride or sodium sulphate, distilled up to 180° to remove ether and traces of moisture. The distillate above 180° is treated with bromine as below.

(*a*) The mixture of phenols is dissolved in water, rendered alkaline with sodium hydrate, and mixed with a known excess of hypobromite solution. The mixture is acidified with hydrochloric acid (1 : 1), vigorously shaken for a minute, potassium iodide added and free iodine titrated with standard thiosulphate solution.

Under these conditions one molecule of ortho-cresol or para-cresol takes up two atoms of bromine, whereas phenol and meta-cresol take up three atoms of bromine.

It is essential that the duration of the experiment does

not exceed a minute, as the para-cresol may take up more bromine.

(*b*) When the alkaline solution of phenols, treated with excess of hypobromite solution, is acidified with concentrated sulphuric acid, allowed to stand for ten minutes, with subsequently five minutes' shaking, and is filtered through glass wool, it is found that ortho- and para-cresols take up three atoms of bromine and that phenol and meta-cresol take up four atoms of bromine.

The filtrate is treated with potassium iodide and the free iodine titrated with standard thiosulphate solution.

Let a = quantity of phenols taken.
x = amount of phenol.
y = amount of mixture of ortho- and para-cresols.
z = amount of meta-cresol.
b = amount of bromine using dilute hydrochloric acid.
c = amount of bromine absorbed when concentrated sulphuric acid is used and the mixture filtered.

Then (i) $x + y + z = a$.
(ii) $3\,\mathrm{Br}/94{\cdot}06 \cdot x + 2\,\mathrm{Br}/108{\cdot}08 \cdot y + 3\,\mathrm{Br}/108{\cdot}08\, z = b$.
(iii) $4\,\mathrm{Br}/94{\cdot}06 \cdot x + 3\,\mathrm{Br}/108{\cdot}08 \cdot y + 4\,\mathrm{Br}/108{\cdot}08\, z = c$.

Bromination of Phenols.

L. V. Redman, A. J. Weith, and F. P. Brock ["J. Ind. and Eng. Chem.," 1913, 5, 389].

Solutions employed :—

$\frac{N}{10}$ bromide-bromate (2·76 gms. $KBrO_3$ and 15 gms. KBr in 1 litre).

$\frac{N}{10}$ sodium thiosulphate.

Twenty per cent KI and 0·5 per cent starch solution.

The bromide-bromate solution is standardized by adding KI solution and titrating the free iodine with the thiosulphate solution.

Place 50 c.c. water, 5 c.c. HCl (sp. gr. 1·2), and 15 c.c. of the phenol solution $\left(\frac{N}{10}\right)$ into a 500 c.c. glass-stoppered bottle. Add slowly, with shaking, sufficient bromide-bromate to impart a slight permanent yellow colour to the solution, the temperature being about 22° C. Replace the stopper and shake continuously for one minute. Now add 0·5 c.c. KI solution, shake for a minute and titrate with thiosulphate, adding the indicator when the colour has almost vanished.

1 c.c. bromide-bromate ≡ 0·00156 gm. phenol.

$KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O$.

Notes on Method :—

1. The acidity must not fall below 0·48 N if the bromination of the phenol is to be complete in one minute ; acidity 0·5 to 1·0 N is advised.

2. A large excess (over 50 per cent) of KI above that necessary for complete reduction of the free bromine, according to the above equation, is not needed.

3. Low temperatures retard the operation, 20°-30° is recommended by the authors.

4. Error in rapid estimations is about 0·00005 gm.

Method of E. Riegler; by formation of a dye.

["Bull. Soc. Sci. Bucuresci," 8, 51].

Preparation of diazo-solution.—Dissolve 5 gms. of para-nitraniline in 25 c.c. water containing 6 c.c. of sulphuric acid. Add to this 100 c.c. of water and 25 c.c. of sodium nitrite solution containing 3 gms. of $NaNO_2$. The whole is then diluted to 200 c.c. with water and stored in a dark place.

Procedure.—20 c.c. of the above solution are added to 50 c.c. of an aqueous solution of phenol containing not more than two gms. per litre, and to the mixture are added 10 c.c. of a 5 per cent sodium hydrate solution. The red coloured solution is acidified with dilute sulphuric acid (1 : 5)

whereby a yellow substance is precipitated. The latter compound is washed, dried at 100° and weighed.

$$C_6H_5 . OH + NO_2 . C_6H_4 . N_2 . Cl = HCl + NO_2 . C_6H_4 . N_2 . C_6H_4 . OH$$

The dye is practically insoluble in water, 100 c.c. dissolving 0·0002 gm.

Estimation of Beta-naphthol.

F. W. Küster [" Ber.," 27, 1905] has drawn up a series of curves to be used in conjunction with the following method of analysis. 100 c.c. of the solution of β-naphthol (containing 0·1 to 0·5 gm. per litre) are mixed with 0·6 c.c. of 3·6 N sodium hydrate and 25 c.c. $\frac{N}{10}$ iodine solution. He used known amounts of substance in a series of experiments and plotted the amounts of standard thiosulphate required to titrate back the residual iodine.

For the tables, reference should be made to the original memoir.

ACIDS.

Estimation of Acetic Acid and Acetates.

Direct Titration Methods.

1. A. Sonnerschein ["Chem. Zeit.," 11, 591].

Methylaniline orange (Orange 4) is changed to red by mineral acids, whereas it is unaffected by acetic acid. Hence, a mixture of acetic acid and mineral acids can be estimated as follows:—

(i) Titrate with standard soda, using litmus as indicator giving total acids.

(ii) Titrate with soda, using methylaniline orange giving the mineral acids only.

The difference between the titration values of (i) and (ii) gives the value of the acetic acid present.

To estimate acetic acid in acetates, 5 gms. of the solid are dissolved in 250 c.c. of water. Fifty c.c. of this solution are titrated with N hydrochloric acid using phenacetoline as indicator.

2. A similar method depending on the colour changes of methylaniline violet with mineral acid and acetic acid has been proposed by G. Witz ["Dingl. polyt. J..," ccxiv. 312].

The author shows that this indicator is changed to bluish-green by small quantities of mineral acid, but is unchanged by acetic acid. The latter is, however, very sensitive to litmus, hence acetic acid may be determined as in the above method.

Using this principle, commercial acetates may be estimated by mineral acids using the methylaniline violet as indicator. With calcium acetate good results are obtained, but in lead acetate the metal must be removed by sodium sulphate before valuation.

3. Acetic Acid in Lead Acetate.

Seward ["Chem. News," 29, 66].

The author dissolves a sample of the acetate in water, adds excess of standard sodium carbonate solution and filters off the lead carbonate precipitate. The contents of the filter are carefully washed and the total filtrates are titrated with standard oxalic acid using litmus as indicator.

Distillation Methods.

1. Acetic acid in presence of inorganic salts, with the exception of nitrates, may be estimated by a method proposed by B. Blount ["Analyst," 22, 309].

The impure acetate is distilled with dilute sulphuric acid till fumes of the latter appear, the distillate being collected in a solution of sodium hydrate. This partially neutralized alkali is then evaporated nearly to dryness, and the sodium acetate and residue of hydrate dissolved out by a large excess of absolute alcohol, in which agent sodium chloride and sulphate are insoluble.

After evaporation of the alcohol, the residue is distilled with dilute sulphuric acid, the distillate being collected in baryta water, excess of the latter being removed by carbon-dioxide. The barium acetate is filtered, washed well, dried and weighed.

2. Acetic Acid in Commercial Acetate of Lime.

A. G. Stillwell [" J. Soc. Chem. Ind.," 1904, 23, 305].

The sample should be kept in closely stoppered jars. To obtain original moisture, it is rapidly passed through a ¼-inch-mesh sieve, dried and weighed. About 6 oz. of an average sample is now forced through a 14-mesh sieve, and the moisture again determined. This constitutes the working sample.

Two gms. are placed in a round bottom flask of 300 c.c. capacity, and with a neck 4 in. long. To this is added 15 c.c. of syrupy phosphoric acid, any drops being carefully washed down the neck with about 25 c.c. of water. The acetic acid is now distilled off and collected in a 12 oz. Erlenmeyer flask containing 30 c.c. of standard sodium hydrate solution. Water is added to the distillation flask through a dropping funnel in order to keep the volume of liquid as near 40 c.c. as possible.

The distillation is carried out for one and a quarter hours, the distillate being exactly neutralized by standard soda from a burette using phenolphthalein, and a small beaker being substituted for the Erlenmeyer flask.

Distil for a further 15 minutes, and add the contents of the beaker to the Erlenmeyer flask. If the colour is discharged, add more soda and distil for another 15 minutes. The distillation should take, normally, one and a half hours.

The standard soda should be made up so that 1 c.c. equals 0·0175 gm. of acetic acid, when 2 gms. are used.

Estimation of Acetic Acid in Commercial Acetate and Separation of Acetic, Propionic, Butyric and Formic Acids.

K. R. Haberland ["Zeit. anal. Chem.," 1899, 38, 217].

This method was adopted for the estimation of acetic acid by the Meeting of Industrial Chemists at Mombach.

10 gms. of the powdered substance are placed in a 300 c.c. flask with 50 c.c. water and are treated with 11 c.c. of hydrochloric acid (sp. gr. 1·124). The mixture is distilled until the residue is syrupy, when 50 to 60 c.c. water are added and the distillation carried to dryness.

In one-fifth of the distillate, the total acids are determined by titration against a normal solution of alkali, using phenol phthalein as indicator, and in one-tenth, the hydrochloric acid is estimated by means of silver nitrate solution. 15 c.c. of pure nitric acid and an excess of standard $\frac{N}{10}$ silver nitrate are added, and the excess of nitrate is found by titration against ammonium thiocyanate solution.

Separation of the homologous acids.—The crude acetate is distilled with phosphoric acid and the distillate evaporated with lead oxide. The residue is dissolved in cold water and the solution heated to boiling. Owing to the insolubility of basic lead propionate in hot water, this compound is precipitated, whereas the remaining salts are soluble and are separated by filtration.

The filtrate is treated with sulphuric acid, evaporated to dryness with excess of zinc oxide and the residue extracted with a large volume of absolute alcohol. Formate of zinc is insoluble in this agent and remains on the filter with lead sulphate. The filtrate is evaporated to dryness and distilled with sulphuric acid, the distillate being treated with silver carbonate. The aqueous solution of silver salts is evaporated on a water bath, when the silver butyrate crystallizes out quantitatively. The silver acetate remains in solution, and may be separated from the crystalline residue.

Special Method for Determining Acetic Acid in Vinegar.

Durien ["J. Pharm.," 1900 (vi), 11, 22].

When the solution is highly coloured, this method may be adopted.

6 c.c. of a solution $\left(\frac{1}{20}\right)$ sodium hydrogen carbonate are introduced into a graduated tube, and 6 cc. of 95° alcohol are carefully added so that the liquids do not mix. One c.c. of a 7 per cent solution of acetic acid is now added, the tube closed with the thumb, shaken, inverted over water, and the volume of evolved gas noted.

A similar experiment is made with the sample of vinegar, and from the volume of gas evolved the percentage of acetic acid present may be calculated, using the data found in the experiment with pure acetic acid.

BENZOIC ACID.

Estimation of Alkali Benzoates.

G. Rebière ["J. Pharm.," 1896, (vi), 3, 113].

The base is estimated by adding to the substance HCl in excess, heating on the water bath until all free acid is removed, and titrating the residual chloride by means of $\frac{N}{10}$ $AgNO_3$ solution.

The benzoic acid is determined in a second and equal portion, which is dissolved in water (50-60 c.c.) and sulphuric acid $\left(\frac{N}{10}\right)$ added, in the exact quantity needed to combine with the metal; the liberated benzoic acid is then titrated with $\frac{N}{10}$ soda, using phenolphthalein as indicator.

With normal benzoates, the quantity of soda required is equal to that of the H_2SO_4 employed, whilst with basic and acid salts it is less and more, respectively.

Ammonium benzoate can be determined by boiling with excess of soda solution and titrating with sulphuric acid.

Benzoic Acid in Fruits and Ciders.

Harry S. Reed ["J. Amer. Chem. Soc.," 1907, 29, 1626].

The sample is acidified with sulphuric acid, the benzoic acid extracted with chloroform and the latter evaporated in a current of air.

The residue is heated at 260° in a current of air and the volatilized benzoic acid absorbed in aqueous NaOH. From this it is recovered by acidifying the solution and shaking with chloroform; the residue left on evaporation is treated with a definite amount of milk of lime and the benzoic acid is calculated from the amount of calcium found in the solution after allowing for dissolved calcium oxide as found by a blank experiment.

The chloroform extract is placed in the reservoir A (Fig. 50). Capacity of A, 50 c.c. Capacity of B, half-filled, 12 c.c.

A is detached, connected to the pump and the $CHCl_3$ allowed to evaporate. A is then placed in a desiccator and when perfectly dry it is attached to B and completely submerged to C in a bath of sand.

B contains normal NaOH and the temperature of the sand is raised to 145°. It is kept at this temperature for a few minutes and finally brought to 260°. The benzoic acid, which sublimes, is drawn by suction through the NaOH and there retained.

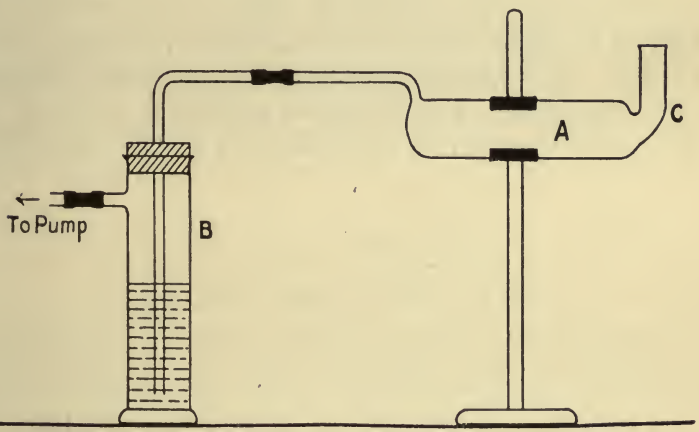


FIG. 50.

Determination.—Add to the benzoic acid residue, 25 c.c. milk of lime containing a known amount of metallic calcium. Use 25 c.c. of this solution of lime also as a blank. Evaporate the mixture to dryness on a water bath. The residue of calcium salts and calcium hydroxide is taken up with 25 c.c. water, filtered and washed with 15 c.c. water. The filtrate is run into a platinum dish and evaporated to dryness. This residue should contain only calcium salts of benzoic and carbonic acids. These are ignited to CaO, which is dissolved in 2 c.c. 2N. HCl and titrated back with $\frac{N}{10}$ NaOH using phenolphthalein.

The amount of calcium in the blank at this stage, is subtracted from that found present in the test and the difference calculated to benzoic acid.

Separation of Salicylic from Benzoic Acid.

Schaap ["Chem. News," 66, 42].

By treating solutions containing these acids with excess of bromine, salicylic acid is wholly precipitated as the dibromo derivative whilst the benzoic acid remains in solution.

In order to directly estimate the benzoic acid, the filtrate is rendered faintly alkaline with sodium carbonate and evaporated to small bulk on the water bath to expel excess of bromine. The residue is acidified with HCl and extracted with chloroform. This is filtered through a dry filter and allowed to spontaneously evaporate on a weighed glass dish.

ESTIMATION OF FORMIC ACID.

Use of Alkaline Permanganate.

1. H. C. Jones ["Amer. Chem. J.," 1895, 17, 539] gives the following method:—

The solution is rendered alkaline with sodium carbonate, warmed, and treated with an excess of standard permanganate solution. The solution is now acidified with sulphuric acid, and an excess of standard oxalic acid run in to destroy the excess of permanganate, and to dissolve the precipitate of manganic oxide. The excess of oxalic acid is now titrated with the original permanganate solution whose strength is known in terms of oxalic acid.

The difference between this and the total amount of permanganate used in the first addition is the equivalent of formic acid present.

2. Method of Erwin Rupp.

["Zeit. anal. Chem.," 1906, 45, 687].

A solution of formic acid (or formate) of strength not greater than 1 per cent, is heated with an excess of $\frac{N}{10}$ permanganate and 0·5 gm. of anhydrous sodium carbonate in a closed flask on a water bath. After 30 minutes' heating, sulphuric acid is added in slight excess. By the addition of crystals, or a strong solution of potassium iodide, iodine is liberated which is titrated with $\frac{N}{10}$ sodium thiosulphate solution.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} \equiv 0{\cdot}0023 \text{ gm. formic acid.}$$

Use of Mercury Salts.

1. Method of A. Leys.

["Chem. News," 1898, **78**, 245].

This method is used for the determination of formic acid in admixture with acetic acid. Dilute, 1 per cent, solutions are advised for the reaction. On the addition of mercuric acetate, crystalline mercurous acetate is produced in quantities proportional to the formic acid present, at ordinary temperatures. This action is hastened on the application of heat and is complete at the boiling-point; it is unaffected by the presence of alcohol, aldehyde or acetic acid.

The total acidity is first found, and if much acetic acid is present, the solution is diluted to 20 or 30 per cent; if, however, the proportion of formic acid to acetic acid is 1 to 20, or greater, the solution is diluted to 2 per cent acidity.

Twenty to thirty c.c. of a 20 per cent solution of mercuric acetate are added to 10 c.c. of the acid solution and the mixture made up to 100 c.c. This latter is then heated during seven or eight minutes to boiling-point and is allowed to cool. The precipitate is filtered off on to a glass wool filter, washed four or five times with 95° alcohol containing 2 per cent of glacial acetic acid, with pure alcohol and, finally, with dry ether.

The residue is dried in air or in a vacuum desiccator, dissolved in nitric acid, and diluted with an equal volume of water and sodium chloride added. The precipitated mercurous chloride is filtered, washed, and dried at 100°. Its weight multiplied by 0·0976 gives the weight of formic acid present.

Should the original solution not contain sufficient acetic acid, 2 c.c. of glacial acetic acid are added before the mercurous acetate.

2. Method of A. Scala.

["Gazzetta," 20, 393.]

An estimation of formic acid in the presence of acetic and butyric acids is carried out as follows :—

The formate solution is weighed into a deep beaker, and an excess of a saturated solution of corrosive sublimate ($HgCl_2$) is added. The beaker is covered with a clock glass and is heated on a water bath for 2 hours. Calomel is precipitated and is collected on a weighed filter, washed with warm water, dried at 100°, and weighed.

If free acid is present in the solution it is neutralized before proceeding as above.

Formic acid precipitates more than ten times its weight of mercurous chloride.

$$H.COOH + 2HgCl_2 = CO_2 + 2HCl + Hg_2Cl_2.$$

3. Method of Portes and Ruyssen.

["Compt. rend.," 82, 1504.]

This can be used in the determination of wood spirit in alcohol. Since formic acid reduces mercuric chloride (in excess) to mercurous chloride, the authors were led to utilize Personne's method, by which a given quantity of sublimate is determined with KI before and after its reduction with a certain quantity of formic acid. As the reaction is slow and not complete, it suffices to add to the solution sodium acetate, which will greatly facilitate the manipulation. Five gms. of sodium acetate are put in a retort with 25 c.c. of the solution to be determined (10 per cent), and 200 c.c. of sublimate (4·5 per cent = 9 gms.) added. The mixture is heated for an hour and a half on a water bath, until the supernatant liquid is perfectly clear; its volume is then made up to 500 c.c. and the solution filtered. By a very simple calculation we obtain numbers for which a correction must be made, as shown by comparative experiments.

Note.—Fin. Sparre ["Zeit. anal. Chem.," 1900, 39, 105]

advocates this method, but points out that the instructions to use the 10 per cent solution must be a misprint for 1 per cent, since the quantity of mercuric chloride mentioned is inadequate for solutions of more than 1 per cent.

Use of Hypobromite.

Method of E. Rupp.

["Arch. Pharm.," 1905, 243, 69.]

Preparation of Hypobromite.—Dissolve 15 gms. of sodium hydrate, purified from alcohol, in about 450 c.c. water in a flask of 500 c.c. capacity. When cool, add 5 c.c. bromine, shake well till dissolved, and dilute to 500 c.c.

To standardize this solution, 5 c.c. are placed in a stoppered bottle and diluted with 50 to 75 c.c. of water. 20 c.c. of 10 per cent hydrochloric acid, and immediately after this, 1 gm. of potassium iodide are added, and when one to two minutes have elapsed, the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate solution.

The solution keeps well in a stoppered bottle if stored in a dark room.

Estimation of Formic Acid.—Dilute a suitable volume of the hypobromite solution to 70 to 100 c.c. with water in a stoppered bottle, and add sufficient formic acid solution to reduce about half the hypobromite. Dilute hydrochloric acid is added drop by drop, until the yellow colour of the bromine is just permanent where the drop falls in, and the vessel is allowed to remain in the dark for half an hour.

Then 1 gm. of potassium iodide and 20 c.c. of dilute hydrochloric acid are added, and the liberated iodine estimated by thiosulphate. The difference between the volume of the thiosulphate now used and that equivalent to the hypobromite solution used measures the amount of formic acid.

$$NaOBr + H.COOH = NaBr + CO_2 + H_2O.$$

Special Methods.

1. Method of F. Freyer.

["Chem. Zeit.," 1895, 19, 1184.]

This process is used in estimating calcium formate in the presence of acetate.

The mixture is treated with dilute sulphuric acid and distilled in a current of steam until the distillate shows no longer any acid reaction. An aliquot part of the distillate is titrated with standard alkali and the total acidity thus determined.

Another portion is exactly neutralized with a solution of sodium hydroxide and is concentrated to small bulk.

The residue is now boiled with a known volume of standard potassium dichromate acidified with dilute sulphuric acid. This completely destroys the formic acid but is without action on the acetic acid present.

The excess of dichromate is afterwards determined in the usual manner by adding potassium iodide and titrating the iodine liberated with standard sodium thiosulphate solution. In order to render the colour change more apparent, a small amount of metaphosphoric acid may be added.

1 molecule of dichromate $\equiv$ 3 molecules of formic acid.

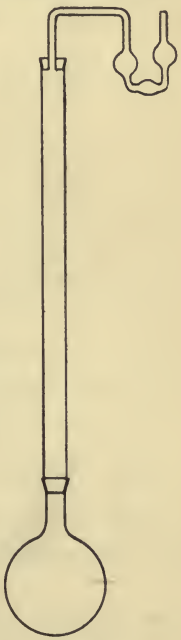


Fig. 51.

2. Method of Béhal.

["Ann. Chim. Phys.," 1900 (vii), 20, 411.]

This method consists in heating the formic acid with iodic acid in concentrated aqueous solution when the following reaction occurs :—

$$2HIO_3 + 5H \cdot CO_2H = 5CO_2 + 6H_2O + I_2.$$

The original apparatus is modified by using a 100 c.c. Jena flask with an air condenser ground in. A set of washing

bulbs containing KI solution is connected to the top end of the condenser (Fig. 51).

The mixture of iodic and formic acids is placed in the flask and gently heated. The liberated iodine is condensed in the air condenser and is washed out by KI solution. The last traces of iodine are removed from the flask by extracting the residue with chloroform and adding the filtered chloroform extract to the main KI solution of iodine. The whole is then titrated with $\frac{N}{10}$ thiosulphate.

0·3718 gm. undiluted formic acid with 20 c.c. of a 50 per cent solution of HIO_3 gave iodine equivalent to 29·31 c.c. $\frac{N}{10}$ $Na_2S_2O_3$ solution.

LACTIC ACID.

Commercial Acid Determination.

Jean ["Ann. Chim. anal. appl.," 1900, 5, 285.]

(i) The total acidity is determined as H_2SO_4.

(ii) Free acids by evaporating three times to dryness on the water bath.

(iii) Lactic acid by evaporating 10 c.c. to dryness several times and dissolving the residue in water. The solution is heated to boiling, neutralized with barium carbonate, filtered and evaporated to dryness in a platinum dish. The residue is ignited producing barium carbonate, extracted with hot water, collected on a filter, washed and finally dissolved in a known excess of standard $\frac{N}{10}$ hydrochloric acid. After being boiled, the solution is titrated with $\frac{N}{10}$ alkali and the amount of $\frac{N}{10}$ HCl neutralized by the carbonate is found by difference.

The number of c.c. × 0·009 = lactic acid present.

Estimation of Lactic Acid in Lactates.

J. Paessler ["Chem. Zent.," 1908, I, 66].

In the absence of other reducing substances, the process is as follows:—

0·4 gm. of the lactate is dissolved in water, 10 c.c. dilute sulphuric acid are added, and the lactic acid is fully oxidized to acetic acid and carbon dioxide by boiling for one hour in a reflux apparatus with addition of 25 c.c. $\frac{N}{2}$ potassium dichromate. When cold, the excess of dichromate is estimated iodometrically. One c.c. of dichromate = 0·01127 gm. lactic acid.

Lactic anhydride is but imperfectly oxidized and should be first digested with a slight excess of alkali hydroxide.

Antimony, if present, should be removed by H_2S and the excess of the latter removed by boiling.

ESTIMATION OF MALONIC ACID.

A. T. Cameron and B. C. McEwan ["Trans. Chem. Soc.," 1910].

Complete oxidation of malonic acid can be brought about by first heating with excess of acid permanganate and then rendering the whole alkaline with excess of alkali which destroys the formic acid.

The sample of acid (0·2 gm.) is added to an approximately 2 N-sulphuric acid solution and excess of permanganate solution. The whole is heated to 80°-90° for 10 minutes, or longer in the case of very dilute solutions. The solution is then rendered alkaline with strong aqueous alkali and the heating continued for some minutes. Then excess of sulphuric and standard oxalic is added and the excess of oxalic determined by permanganate.

$$C_3H_4O_4 + 2O_2 = 2H_2O + 3CO_2.$$

ESTIMATION OF OXALIC ACID.

Use of Potassium Permanganate.

1. By means of a pipette, 25 c.c. of the solution of oxalic acid or oxalate (which should be about tenth normal) are placed in a beaker, 10 c.c. of dilute sulphuric acid (1 : 4) are added; the solution is diluted with water and heated to a temperature of about 70° C. Deci-normal permanganate is run into this solution, with constant stirring, from a burette. The end point is reached when a faint permanent red colour is imparted to the solution.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

2. In the Presence of Hydrochloric Acid.

Baxter and Zanetti ["Amer. Chem. J.," 1905, 33, 500].

The addition of manganous sulphate has been shown to be unnecessary, provided the operation is carried out under well-defined conditions.

About 0·3 gm. of oxalic acid is dissolved in 20 c.c. of hydrochloric acid (sp. gr. 1·04) and diluted with water to 150 c.c. The solution is heated to 70° C. and a standardized solution of permanganate (4 gms. in 1000 c.c.) is run in slowly, with constant stirring until the end point is reached as in the above method.

Special Methods.

1. Method of Jean and Pellet ["Bull. Soc. Chim." (2), 27, 204].

Neutralize the solution of oxalic acid or oxalates with normal soda, add baryta water, and filter the solution. The filtrate is now treated with carbonic acid water, boiled, and the barium carbonate filtered off. The filtrate from this is titrated with normal sulphuric acid, and the amount of oxalate then calculated.

The barium oxalate is filtered off before adding the carbonic acid as otherwise it would vitiate the result owing to decomposition.

$0{\cdot}0777\ H_2SO_4 \equiv 0{\cdot}1$ gm. oxalic acid.

2. Oxalic Acid in Beet Leaves.

Karl Bülow ["Chem. Cent.," 1900, 1, 374].

Five gms. of leaves are treated in a mortar with 5 c.c. of 22 per cent sulphuric acid and 5-6 gms. of powdered pumice. The mixture is extracted with ether in an extraction tube, filtered, and placed with 50 c.c. water in a beaker. The mixture is put in a warm place until the ether has evaporated. The aqueous portion is filtered, neutralized with ammonia, acidified with acetic acid, and precipitated with calcium acetate. The calcium oxalate is freed from sulphate by repeated solution in hydrochloric acid and reprecipitation with ammonia.

ESTIMATION OF PICRIC ACID.

E. Feder ["Zeit. Nahr. und Genussm.," 1906, 12, 216].

(*a*) In aqueous solution picric acid may be estimated by titration with $\frac{N}{10}$ sodium hydrate solution provided sufficient phenolphthalein is used as an indicator.

$$1 \text{ c.c. } \frac{N}{10} \text{ alkali} \equiv 0{\cdot}0229 \text{ gm. picric acid.}$$

(*b*) Add to an aqueous solution a mixture of potassium iodide and potassium iodate. By this method an equivalent amount of iodine is liberated which is titrated against standard thiosulphate solution in the usual manner using a solution of starch as indicator. The end point is quite distinct, the colour changing sharply from greenish-blue to a pure yellow. In the estimation of picrates, the acid is liberated by the addition of hydrochloric acid and is extracted with benzene.

$$1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} \equiv 0{\cdot}0229 \text{ gm. picric acid.}$$

ESTIMATION OF SALICYLIC ACID.

A critical examination of the methods of analysis of salicylic acid has been made by Fresenius.

The usual methods are: (*a*) By extraction; (*b*) iodometric; (*c*) bromometric; (*d*) colorimetric.

(*a*) The investigator purified a quantity of sodium salicylate and confirmed the purity thereof by estimating the sodium.

0·3017 gm. of this pure compound was dissolved in 30 c.c. water, excess of sulphuric acid added and the salicylic acid extracted with four successive portions (25 c.c.) of chloroform. The extracts were washed, evaporated at low temperature, and dried in a water oven. From a series of results it is concluded that this method gives only approximate values.

The residues were then dissolved in ether before being dried in the oven, which was kept at a lower temperature. Even with this more volatile solvent varying results were obtained as it was found impossible to find out when the solvent had evaporated.

M. Saupe ["Pharm. Cent.," 31, 314] has obtained good results for fatty acids by drying them on the top of the water oven, and not in it. This method was tried in the case of salicylic acid, but high results were obtained.

Best results were obtained by using a solvent composed of equal parts of ether and petroleum spirit.

(*b*) An iodometric method has been suggested by Messinger and Vortmann ["Ber.," 1890, 22, 2312].

An alkaline solution is heated at 50°-60°, and excess of a standard iodine solution added. The mixture is heated again to 60° when a red precipitate is produced, the latter being increased by an addition of dilute sulphuric acid in excess. When cold the mixture is made up to definite volume, filtered, and excess of iodine titrated in the usual manner.

The first formula put forward by Messinger and Vortmann shows that salicylic acid accounts for 4 atoms of iodine.

$$C_6H_4(OH).COOH + 2I_2 = C_6H_3I(OI).COOH + 2HI$$

Later, Vortmann made use of the following :—

$$C_6H_4(OH) \cdot COONa + 3NaOH + 3I_2 =$$
$$C_6H_2I_2(OI) \cdot COONa + 3NaI + 3H_2O$$

The investigator found this method unreliable as the exact conditions of quantitative work are unknown.

(*c*) Best results were obtained with the following method due to Freyer ["Chem. Zeit.," 1896, **20**, 820].

This is based upon Koppeschaar's method for the estimation of phenol.

$$C_6H_4\begin{<}{OH \atop CO_2H} + 4Br_2 = C_6H_2Br_3 \cdot OBr + 4HBr + CO_2$$

$$C_6H_2Br_3 \cdot OBr + 2KI = C_6H_2Br_3OK + KBr + I_2$$

Hence 6 atoms of bromine $\equiv$ 1 molecule of salicylic acid.

The best results were obtained as follows:—

A bromine solution was made up by dissolving 3 gms. of sodium bromate and 20 gms. of sodium bromide in a litre of water.

This is standardized by adding potassium iodide and hydrochloric acid and then titrating the iodine produced.

Procedure.—The required amount of the above bromine solution is diluted with 300 c.c. water and decomposed by 30 c.c. of hydrochloric acid (sp. gr. 1·10).

To this is added with constant stirring a solution of about 1 per cent strength of the substance under examination.

A white precipitate is formed, and after standing 5 minutes with occasional agitation 30-40 c.c. of a 10 per cent potassium iodide solution are added, and the iodine liberated is titrated with standard thiosulphate solution.

In the analysis of wines sulphurous acid is sometimes present; the sample is rendered alkaline, concentrated, rendered acid, and extracted with ether and petroleum spirit. The extract is shaken with alkali and estimated as above.

(*d*) Salicylic acid may be estimated colorimetrically by means of ferric chloride. The investigator found that the amount of acid must be less than 2 mgs.

Estimation of Salicylic Acid in Admixture with Cinnamic Acid.

J. Bougault [" Compt. rend.," 1908, 146, 1403].

Fifty c.c. of the aqueous solution containing about 0·1 gm. of salicylic acid are treated with 1 gm. of sodium carbonate and excess of iodine solution. The mixture is heated for 20 minutes on the water bath, finally being boiled for about 10 minutes under a reflux apparatus. During the latter operation iodine is added occasionally to ensure excess being present.

The excess of iodine is now destroyed with sodium sulphite solution, and the precipitate collected on a Gooch crucible.

Weight of precipitate × 0·40116 = weight of salicylic acid.

SUCCINIC ACID.

Succinic acid may be estimated in the presence of tartaric and lactic acids by the method of Bordas, Joulin, and Raczkowski ["J. Pharm. Chim.," 1898, **7**, 417; "Chem. News," **78**, 18].

The solution is exactly neutralized with $\frac{N}{10}$ KOH, excess of $AgNO_3$ solution added, and the precipitate washed until all soluble silver salts have been removed. The precipitate of silver succinate is washed into a flask with water, and titrated with NaCl solution until the red colour produced by two drops of potassium chromate disappears. The solution is then titrated back with $\frac{N}{10}$ silver nitrate solution.

Estimation in presence of citric acid and tartaric acid —see Micko ["Zeit. anal. Chem.," **31**, 465].

TARTARIC ACID.

The tartrate may be ignited to produce either an oxide or carbonate. Excess of acid is added to dissolve the residue, and standard alkali is run in to neutralize the excess of acid.

Free Tartaric Acid.

Allen [" Chem. News," 1875, 31, 277].

Two gms. of the sample are dissolved in 20 c.c. proof-spirit. This is filtered and the filtrate made up to 45 c.c. with additional proof-spirit. This solution is treated with 5 c.c. of a cold saturated solution of potassium acetate and stirred for ten minutes. The crystals of acid potassium tartrate are filtered and washed with alcohol. The precipitate may be dissolved and titrated with $\frac{N}{10}$ alkali, using phenolphthalein as indicator, or washed into a dish with hot water and evaporated. It is finally dried at 100° and weighed.

ALDEHYDES.

Estimation of Formaldehyde.

Suggestive reactions in which formaldehyde plays a part are as follows :—

(*a*) $H.CHO + H_2O_2 + NaOH = H.COONa + 2H_2O$.

(*b*) $H.CHO + I_2 + NaOH = 2NaI + H.CO_2H + H_2O$.

(*c*) $3CH_2O + KClO_3 + AgNO_3 = AgCl + 3CH_2O_2 + KNO_3$.

(*d*) $CH_2O + C_6H_5.NH_2 = C_6H_5.N:CH_2 + H_2O$.

(*e*) $CH_2O + NH_2.OH, HCl = CH_2:NOH + HCl + H_2O$.

(*f*) $2CH_2O + NaOH = H.CO_2Na + CH_3.OH$.

(*g*) $CH_2O + KCN = N \vdots C.C\begin{matrix}H_2. \\ O_2K.\end{matrix}$

(*h*) $6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O$.

I.—Methods Involving the Use of Ammonia.

A. Trillat ["Compt. rend.," 116, 891].

A measured volume of the solution is first neutralized by means of sodium hydrate solution, using phenolphthalein as indicator. The acidity is thus determined.

Ten c.c. of the solution are diluted and mixed with a known excess of standard ammonia solution. After standing for some time with the flask corked, the mixture is steam distilled, the distillate being collected in a known volume of standard acid. The amount of ammonia combined with the aldehyde can be now determined, and by using formula (*h*) above, the quantity of formaldehyde present in solution is calculated.

A little of the amine is volatilized in the above process.

Method of Legler.

["Ber.," 16, 1333.]

Five c.c. solution are placed with 20 c.c. water and 10 c.c. N. ammonia solution in a stoppered bottle. The mixture is allowed to stand for one hour, and then 20 c.c. of normal hydrochloric acid solution are added. The excess of acid is then titrated with normal potassium hydroxide solution, using rosolic acid as indicator.

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

For a criticism of this method see Kippenberger ["Zeit. anal. Chem.," 1903, 42, 694].

Method of A. G. Craig.

["J. Amer. Chem. Soc.," 1901, 23, 638.]

The author modifies Legler's method as follows:—

A weight of the sample containing about 0·5 gm. of pure aldehyde is placed in a 3-oz. pressure bottle fitted with a rubber stopper, with 25 c.c. of standard ammonia solution (approximately $\frac{N}{1}$).

A similar volume of ammonia solution is also placed in a pressure bottle, and both are immersed to the neck in boiling water for an hour. After cooling, both are titrated with normal sulphuric acid, using methyl orange as indicator. The difference between the determinations gives the amount of ammonia combined with the aldehyde.

$$1 \text{ c.c.} \equiv 0{\cdot}0601 \text{ gm. aldehyde.}$$

A criticism of Legler's method has been made by Z. Peška ("Chem. Zeit.," 1901, 25, 743). He states that good results are obtained if the excess of ammonia is titrated, using litmus as indicator, the end point being observed by noting the disappearance of the blue colour and not by waiting for the generally accepted neutral colour.

II.—Oxidation Method.

Harry M. Smith ["Analyst," 1896, 21, 148].

Aqueous potassium hydrate is added to a volume of the sample until the amount of alkali is about 10 per cent.

A standard permanganate solution (5·26 gms. to the litre) is now slowly run in until the green colour vanishes, rather slowly.

The mixture is now carefully heated to 30°, which causes the precipitate to settle. The permanganate is again added, very slowly, until an olive-green colour is produced, which is permanent for 15-20 seconds.

1 c.c. permanganate ≡ 0·0015 gm. aldehyde.

To obtain confirmatory data respecting the above determination the mixture is now boiled and permanganate run in until the formic acid is entirely destroyed. This is shown when an emerald-green colour lasting for 10 minutes is obtained :—

1 c.c. permanganate ≡ 0·0075 gm. aldehyde.

III.—Methods of Gysbert Romijn.

["Zeit. anal. Chem.," 1897, 36, 18.]

1. This first method is based upon the reaction (*b*) indicated above.

Ten c.c. of the commercial formaldehyde solution, containing 40 per cent of formaldehyde, are diluted to 400 c.c. and 5 c.c. taken for analysis. To this solution are added 25-40 c.c. of $\frac{N}{10}$ iodine solution, and so much strong sodium hydroxide solution, drop by drop, that the liquid assumes a light yellow colour. After a period of 10 minutes the solution is acidified with hydrochloric acid, and free iodine titrated back with $\frac{N}{10}$ thiosulphate solution.

1 c.c. $\frac{N}{10}$ iodine solution ≡ 0·001501 gm. formaldehyde.

Peška states this method is very satisfactory.

2. The second method is based upon reaction (*g*).

A standard solution of potassium cyanide is made by dissolving 6 gms. in a litre of water. A quantity of this solution, in excess of that required by the equation, is added to a dilute solution of the aldehyde. This mixture is then thrown into an excess of $\frac{N}{10}$ silver nitrate rendered acid with nitric acid so that after addition of the cyanide the mixture remains acid. The excess of silver nitrate is now estimated by Volhard's method :—

1 molecule potassium cyanide is equivalent to 1 molecule of formaldehyde.

Notes.—If acetaldehyde is present the mixture must be immediately mixed with excess of silver nitrate. Acetone and benzaldehyde do not affect the reaction.

Formaldehyde in the Presence of Hexamethylene Tetramine.

H. A. B. Dunning ["Amer. J. Pharm.," 1913, **85**, 453].

Small quantities of formaldehyde are estimated as follows :—

Five c.c. sample are mixed with 0·1 c.c. 15 per cent NaOH solution, then with 0·1 c.c. phenylhydrazine (base) and 0·7 gm. solid NaOH. The whole is shaken for 10 minutes and compared colorimetrically with standard solutions of formaldehyde treated in the same manner.

Dextrose, acetone, and acetaldehyde do not interfere in solutions of formaldehyde weaker than 1 in 30,000.

ACETALDEHYDE.

(*a*) Neutral Sulphite Method.

Seyewetz and Bardin [" Bull. Soc. Chim.," 1905 (3), 33, 1000].

A solution is diluted so that it contains not more than 7-8 per cent of the aldehyde and cooled to 4°-5°. Ten c.c. of this solution are added to 40 c.c. of a 10 per cent solution of sodium sulphite containing one drop of a 0·2 per cent alcoholic solution of phenolphthalein. Add acid to exactly neutralize the solution and then titrate the neutral solution with standard H_2SO_4. The acid sulphite produced forms a compound with the aldehyde which is neutral to phenolphthalein. After the whole of the aldehyde has been thus combined the next drop of acid liberates free $NaHSO_3$, which immediately colours the indicator.

The equation expressing this action is

$$2Na_2SO_3 + 2CH_3CHO + H_2SO_4 = 2(NaHSO_3 + CH_3CHO) + Na_2SO_4$$

Alcohol, paraldehyde and acetal have no appreciable influence on the action, but acetic acid, if present, must of course be separately determined.

Trioxymethylene and formaldehyde (in 0·01 per cent solutions) can also be accurately estimated by this method. See Seyewetz and Gibello [" Bull. Soc. Chim.," 1904 (3), 31, 691].

(*b*) Bisulphite Method.

Rocques [" J. Pharm. Chim.," 1898, 8 (9), 390].

12·6 gms. of pure sodium sulphite are dissolved in water, 100 c.c. N . H_2SO_4 added, and made up to 1 litre with 96 per cent alcohol. This solution is allowed to stand twenty-four hours and then filtered.

To 10 c.c. aldehyde solution 50 c.c. of the bisulphite are added, and made up to 100 c.c. with 50 per cent alcohol, the whole then well shaken. A blank is set going at the same time by diluting 50 c.c. of the bisulphite solution with 50 c.c. of 50 per cent alcohol. Both flasks are left for twenty-four

hours at the ordinary temperature, again well shaken and titrated against $\frac{N}{10}$ iodine.

1 c.c. $\frac{N}{10}$ iodine $\equiv 0{\cdot}0022$ gms. acetaldehyde.

This method can be used for acetaldehyde of strengths between 1·0 and 2·0 per cent. If the content of the solution is below 1 per cent, the bisulphite and iodine should be diluted accordingly. Paraldehyde forms no bisulphite compound so that its presence does not affect the method.

Later, the same author slightly modified the conditions by raising the temperature and thus shortening the time ["Comp. rend.," **127** (20), 765].

Ten c.c. of the aldehyde solution are placed in a 100 c.c. flask with a known volume of the alcoholic bisulphite and made up to 1 litre. In a similar flask are placed the same quantity of bisulphite solution and made up to mark with 50 per cent alcohol. Both flasks are heated on the water bath at 50° for four hours, then cooled and titrated, and the aldehyde corresponding to the difference calculated.

The limits for accurate results are 0·5 and 2·0 per cent.

BENZALDEHYDE AND OIL OF BITTER ALMOND.

F. D. Dodge ["Eighth Int. Cong. App. Chem.," 1912, 17, 15].

The following methods yield trustworthy results :—

The hydrazone method.
Bennett's oxime method [Analyst, 1909, 34, 14].
Sodium hydrogen sulphite method.

It is essential in the latter to maintain the temperature of the reacting substances at 0°, the time of contact being two hours.

Approximately correct results are also obtained as follows :—

The aldehyde solution is treated with excess of 2·5 N potash solution, and after remaining some twenty-four hours, the excess is titrated with $\frac{N}{2}$ hydrochloric acid.

$$2C_6H_5 . CHO + KOH = C_6H_5 . CO_2K + C_6H_5 . CH_2OH.$$

The presence of HCN interferes somewhat in any of the methods when applied to oil of bitter almonds.

Other methods are given below.

Estimation of Benzaldehyde.

1. Method of B. G. Feinberg.

["Eighth Int. Cong. App. Chem.," 1912, 1, 187.]

This estimation depends on the use of *p*-nitrophenylhydrazine. The aldehyde is dissolved in acetic acid, so that the solution contains about 0·25 gm. in 75 c.c. of 4 per cent acetic acid. About twice the theoretical amount of *p*-nitrophenylhydrazine is dissolved in 30 c.c. of 30 per cent acetic acid, and this solution added to that of the benzaldehyde. The mixture is left to stand for five hours, and is then filtered on a Gooch filter, washed with 10 per cent acetic acid, and dried at 105°.

1 gm. precipitate ≡ 0·440 gm. benzaldehyde.

Results show that the benzaldehyde may be under-estimated by 1·2 ± 0·7 per cent. See also p. 127.

2. Method of H. Hérissey.

["J. Pharm. Chim.," 1906 (vi), 23, 60].

The estimation of small amounts of benzaldehyde from saturated solutions as benzaldehyde phenylhydrazone may be made as follows :—

The mixture of aldehyde and phenylhydrazine is heated for 20 minutes at 100°. It has been shown that in the cold the precipitation is not complete even after 24 hours, but by heating the mixture good results are obtained.

ESTIMATION OF VANILLIN.

1. By Precipitation as Hydrazone.

Hanus ["Zeit. Unters Nahr. Genussm.," 1900, 3, 536].

0·5 gm. of p-bromphenylhydrazine (i.e. two to three times the theoretical amount) is dissolved in 75 c.c. of hot water and added to 25 c.c. of a 1 per cent solution of vanillin previously warmed. During precipitation it is advisable to keep the temperature at about 50°. After four or five hours, filter on to a Gooch, wash with hot water until the washings fail to reduce a solution of silver nitrate, dry at 100° and weigh.

Weight of hydrazone × 0·4739 = weight of vanillin.

See also p. 127 (Feinberg on aldehydes).

2. Titration Method.

Wellman ["Pharm. Zeit.," 1898, 634].

One gm. of vanillin is put into a 200 c.c. stoppered flask with 25 c.c. alcohol and 25 c.c. $\frac{N}{2}$ alcoholic potash. The excess of alkali is back titrated with $\frac{N}{2}$ acid using phenolphthalein as indicator. The strength of the alcoholic potash with addition of an equal volume of alcohol is determined and the difference in the two titrations multiplied by 0·076 ≡ weight of vanillin.

$$CH_3O \cdot C_6H_3(OH) \cdot CHO + KOH = CH_3O \cdot C_6H_3(OK) \cdot CHO + H_2O$$

3. Analysis of Vanilla Extract.

A. L. Winton and M. Silvermann ["J. Amer. Chem. Soc.," 1902, 24, 1128].

Twenty-five grams of the extract are freed from alcohol on the water bath, precipitated by the addition of N. lead acetate and filtered. After washing the precipitate with hot water, the cooled filtrate is extracted with ether using 20 c.c. of the latter at a time. The vanillin is separated from the combined ether extracts by shaking four or five times with ammonia (2 per cent). The ethereal solution containing coumarin is evaporated, dried in a desiccator and weighed. It is advisable to extract the coumarin with light petroleum and deduct the insoluble residue. Melting-point of coumarin should be 67°.

Acidify the ammoniacal solution with HCl and extract repeatedly with ether. Evaporate the extract, dry the residue over sulphuric acid, and weigh. Extract the vanillin with boiling light petroleum and deduct the insoluble residue. Vanillin has a melting-point of 80°-81°.

ACETONE.

Acetone may be estimated accurately by several of the general methods for compounds containing the carbonyl group given in Chapter III. The nitrophenylhydrazine method, for example, gives good results. The conditions for the bisulphite method have been worked out by Jolles. The specific methods in use depend on :—

(1) The formation of an insoluble mercuric complex.
(2) The production of iodoform.
(3) The production of bromoform.

These are treated in order.

Adolf Jolles ["Ber.," 1906, 39, 1306].

A known volume of about $\frac{N}{5}$ sodium bisulphite solution freshly prepared, and being three to four times the theoretical amount, is added to the acetone solution (0·2 per cent) which is then allowed to stand for 30 hours. The excess is then titrated against $\frac{N}{10}$ iodine. A similar quantity of the bisulphite was allowed to stand for the same time and titrated. The difference corresponds to the weight of acetone present.

$$CH_3 . CO . CH_3 + NaHSO_3 = (CH_3)_2C\begin{matrix}OH\\ \diagup\\ \diagdown\\ SO_3Na\end{matrix}$$

1. Georges Denigès ["Comp. rend.," 1898, 127, 963].

Acetones of the fatty series, treated with very great excess of mercuric sulphate, give insoluble, or very slightly soluble compounds. If such compounds are dried at 110° for a long time they approximate to the general formula $(HgSO_4)_2 . 3HgO . COR'_2$. If, however, they are dried in vacuo, they correspond rigorously to $(2HgSO_4 , 3HgO)_3 , 4COR'_2$.

The high molecular weight of such compounds, 3952 in the case of acetone, permits of using very small quantities

of the ketone. The method can be applied either volumetrically or gravimetrically.

(*a*) *Gravimetric Process.*—The precipitating reagent is prepared by dissolving 5 gms. mercuric oxide in a cold mixture of 20 c.c. concentrated H_2SO_4 and 100 c.c. water.

Into a strong flask of 100 c.c. capacity put 25 c.c. of the mercury solution and 25 c.c. of the acetone solution which must not contain more than 0·05 gm. acetone. Wire in the stopper and place the flask in a water bath and bring the temperature to 100°, maintaining it for 10 minutes. Cool, filter on a tared paper, wash with cold water, dry in vacuo and weigh. The weight of precipitate × 0·06 (theoretical coefficient is 0·0584) gives the weight of acetone in the 25 c.c. of solution taken.

(*b*) *Volumetric Process.*—The contents of the flask after treatment with the mercuric solution at 100° for 10 minutes are made up to 100 c.c., 20 c.c. are withdrawn and filtered, 15 c.c. of NH_4OH (1 : 5), 50 c.c. water and 10 c.c. of $\frac{N}{10}$ KCN solution are added, and the whole titrated against $\frac{N}{10}$ $AgNO_3$ using KI as indicator.

If n = volume $\frac{N}{10}$ $AgNO_3$ solution.

x = quantity of acetone per litre of solution used.

$x = (n - 0{\cdot}4) \times 0{\cdot}3$ gms.

Methyl alcohol must not be present in amounts above 10 per cent and ethyl alcohol not above 1 per cent.

2. Method of J. Messinger ["Ber.," 1888, 21, 3366].

Acetone in Methyl Alcohol.—Iodine in alkaline solution reacts with acetone producing iodoform.

$$2CH_3 . CO . CH_3 + 12KIO = 2CH_3 . CO . CI_3 + 6KOH + 6KI$$

$$2CH_3 . CO . CI_3 + 2KOH = 2CHI_3 + 2CH_3\,COOK$$

This reaction can be used for quantitative work, the excess of iodine being decomposed according to the equations

$$I_2 + 2KOH = KIO + KI + H_2O$$

$$KIO + KI + 2HCl = I_2 + 2KCl + H_2O$$

Twenty to thirty c.c. of N . KOH (free from nitrite) and 1-2 c.c. of the methyl alcohol sample are well shaken up in a 250 c.c. stoppered flask. 20-30 c.c. of $\frac{N}{5}$ iodine solution are run in from a burette and the whole shaken half a minute until the solution becomes clear. The solution is acidified with HCl (sp. gr. 1·025), an excess of $\frac{N}{10}$ thiosulphate added, and the excess titrated with $\frac{N}{5}$ iodine solution using starch solution as indicator. Each molecule of acetone requires 3 molecules of iodine to give iodoform.

Using solution of the exact strengths given
if r = number of c.c. iodine required
n = number of c.c. of alcohol sample used (usually 1 or 2).
Then the weight of acetone in 100 c.c. alcohol solution

$$= \frac{r}{n} \times 0{\cdot}19334.$$

Vaubel and Scheuer ["Zeit. angew. Chem.," 1905, **18**, 214] prefer to titrate the excess of iodine with standard arsenious acid in presence of sodium bicarbonate.

W. M. Marriott ["J. Biol. Chem.," 1913, **16**, 281] considers this method to be quite accurate even in dilute solutions.

Method of Robineau and Rollin ["Mon. Sci." (4), **7**, 272].

The acetone is converted to iodoform by dissolving in aqueous NaOH containing KI and adding a standard solution of sodium hypochlorite until a drop of the mixture gives a blue colour on starch paper.

Five hundred c.c. of concentrated commercial sodium hypochlorite are diluted to 1 litre and 10 c.c. concentrated NaOH solution added. This solution is kept well corked.

Standardization of Hypochlorite Solution.—Two gms. of pure acetone (from bisulphite compound) are weighed out and diluted to 500 c.c. To 100 c.c. of this, 10 gms. pure KI are added together with 20 c.c. NaOH solution (sp. gr. 1·24). Hypochlorite solution is run in from a burette drop by drop,

with constant stirring. The iodoform at first crystallizes out in large flakes. When further additions of hypochlorite give only slight cloudiness the solution is tested by bringing a drop on a glass rod in contact with a drop of starch solution containing sodium bicarbonate. As soon as the blue colour is obtained the hypochlorite is in excess.

Each molecule of acetone is equivalent to 6 atoms of available chlorine in the hypochlorite solution. Instead of using acetone the available chlorine content may be estimated directly by any of the common methods.

Methyl and ethyl alcohol do not affect the method, neither does paraldehyde unless present in considerable amount.

Modification of Robineau and Rollin's Method. By Kebler ["J. Amer. Chem. Soc.," 1897, 19, 316].

The solutions required are :—

(1) HCl 6 per cent solution.

(2) $\frac{N}{10}$ thiosulphate.

(3) Alkaline KI solution : 257 gms. NaOH are dissolved in water and made up to 1 litre. After standing, 800 c.c. of the clear solution are added to 1 litre of KI solution containing 250 gms. KI.

(4) Hypochlorite solution : 100 gms. of bleaching powder (35 per cent available chlorine) are mixed with 400 c.c. water. A hot solution of 120 gms. crystallized Na_2CO_3 in 400 c.c. water is added. After cooling, the clear liquid is separated by decantation and filtration, and made up to 1 litre ; 25 c.c. of NaOH solution (sp. gr. 1·29) are added to each litre of solution.

(5) Aqueous solution of acetone (1-2 per cent).

(6) Bicarbonate starch solution : 0·125 gm. starch is treated with 5 c.c. cold water, 20 c.c. boiling water added, boiled for a few minutes, and 2 gms. $NaHCO_3$ added.

Estimation.—10 c.c. of the aqueous acetone solution are added to 20 c.c. of KI solution and a known excess of hypochlorite solution run in from a burette. The mixture is well shaken and acidified with the HCl, and an excess of the thio-

sulphate solution added whilst still shaking. The whole is allowed to stand for some minutes, starch solution added, and the excess of thiosulphate back titrated. Knowing the strength of the hypochlorite solution in terms of the thiosulphate the amount of acetone is readily calculated.

3. Method of Samuel M. Auld ["J. Soc. Chem. Ind.," 1906, 25, 100].

A quantity of solution containing 0·1-0·2 gm. acetone is diluted with water and mixed with 20-30 c.c. of a 10 per cent KOH solution in a 500 c.c. round-bottomed flask provided with a reflux apparatus and a dropping funnel. A solution of bromine containing 200 gms. pure bromine and 250 gms. KBr per litre, is added from the dropping funnel until the contents of the flask assume a faint yellow colour. The flask is now heated on the water bath at 70° for half an hour. Excess of bromine is destroyed with a few drops of KOH solution. The mixture is distilled until no more bromoform is carried over, halogen being tested for in usual manner, and the distillate with condenser washings are mixed with 50 c.c. of alcohol and KOH to make a 10 per cent solution.

The mixture is transferred to a reflux apparatus and heated on the water bath until the bromoform is completely decomposed (three quarters of an hour).

$$3CHBr_3 + 9KOH + C_2H_5OH = 3CO + C_2H_4 + 9KBr + 7H_2O.$$

The liquid is cooled, exactly neutralized with dilute nitric acid, made up to half a litre, and titrated with $\frac{N}{10}$ silver nitrate with potassium chromate as indicator.

240 parts bromine $\equiv$ 58 parts acetone.

The method can be used for the estimation of acetone in wood-spirit by using 5 c.c. of a solution of the spirit diluted to ten times its volume.

AMINES.

Estimation of Aniline, Toluidine, etc.

The general methods for the determination of amines have been already described in Chapter III.

A few special methods are dealt with in the following pages, including one for the estimation of mixtures of aniline and toluidine.

Aniline.

Method of P. Julius ["J. Soc. Chem. Ind.," 9, 109].

In this, aniline is titrated with standard acid in the presence of Congo red. This indicator, the compound of tetrazo-diphenyl with naphthol-sulphonic acid, is turned blue by acids, and recovers its red colour in excess of alkali. When used in titrating aniline or its homologues with a mineral acid, the point is taken at which a bluish-violet colour, unchanged by further additions of acid, is produced.

It is found that a large excess of acid is required to produce the pure blue colour.

Accuracy: Not more than 0·2 per cent error.

Method of M. François ["J. Pharm.," 1899 (vi), 9, 521].

If bromine water is added to an aniline solution which contains a little sulphate of indigo as an indicator, the bromine is without action on the indigo, until all the aniline has been converted into tribromaniline.

The standard solution of bromine water is prepared by dissolving 5 gms. bromine in a litre of water. This is standardized against a known solution of aniline hydrochloride in water made by dissolving 1·392 gms. of pure salt in a litre of water. This solution is of such a strength that 1 c.c. = 0·001 gm. aniline. Special precautions are necessary in the case of the storage of standard bromine solutions. It is essential:—

(1) To use a burette of such capacity that it contains sufficient bromine water for both standardization and estimation determinations without refilling.

(2) To close the end of the burette by a plug of cotton wool.

(3) To find approximately the number of c.c. of bromine water required, and then, in the final determination, to run in the whole almost at once, in order to avoid losses of bromine.

This method may be used in the estimation of aniline hydrochloride, the degree of dilution not influencing the result.

The presence of ammonium salts does not vitiate the results. Should the solution contain mineral substances which react with bromine, the aniline is liberated by potash, distilled in steam and estimated in the distillate.

Estimation of Small Amounts of Aniline in Toluidine and of Toluidine in Aniline.

P. Dobriner and W. Schranz ["Zeit. anal. Chem.," 1895, **34**, 734].

It has been shown by Reinhardt ["Chem. Zeit.," **17**, 413] that the proportions of aniline and toluidine in a mixture of the two can be calculated from the amount of bromine absorbed when a solution of the bases in HBr is treated with a mixture of potassium bromide and bromate, obtained by dissolving bromine in potash, and boiling the solution until free from hypobromite.

Aniline is converted into a tribromo derivative, whilst the toluidines yield dibromo derivatives.

Let a = weight mixture.

v = volume bromine solution.

t = its titre referred to pure aniline.

x = amount aniline present.

then $x = 2{\cdot}37\ vt - 1{\cdot}37\ a$.

Since the strength of the bromine solution is ascertained by experiments on pure aniline, the above formula is calculated on the assumption that 160·5 parts of toluidine absorb as much bromine as 93 parts of aniline, and for mixtures in

which the aniline predominates, this assumption is sufficiently accurate.

When toluidine is the chief factor, the bromine solution must be standardized against pure toluidine.

Let t and T be the titres for aniline and toluidine respectively

$$V = \frac{x}{t} + \frac{a - x}{T}.$$

The end point of the bromination is ascertained by using starch-iodide paper.

In the case of *p*-toluidine it is necessary to add the bromine solution slowly.

Estimation of Trimethylamine in Presence of Ammonia. K. Budai ["Zeit. physiol. Chem.," 1913, 86, 107].

The method is based upon the fact that the trimethylamine will not react with formaldehyde. The aqueous mixture of hydrochlorides is treated with an excess (10 c.c.) of formaldehyde (made neutral to phenolphthalein) and titrated with $\frac{N}{10}$ caustic alkali using phenolphthalein as indicator. This estimates the ammonia present.

The total nitrogen is estimated as follows: The liquid after titration is diluted, acidified with HCl, boiled down to one-third its volume, made alkaline, and distilled into a known amount of acid $\left(\frac{N}{10}\right)$.

c.c. $\frac{N}{10}$ HCl × 1·4 = mg. tertiary amine nitrogen.

CHLOROFORM.

Method of William A. Puckner ["Arch. Pharm.," 1901, 4, 124].

Estimation of Chloroform in Ether.—A quantity of the mixture equal to not more than 0·2 gr. chloroform is put into a strong flask containing 10 c.c. of N alcoholic potassium hydrate free from chlorine, the flask is closed with a sound cork, covered with cloth and tied down securely. The liquids are mixed and the flask is immersed in boiling water for 3 hours.

When cold, the contents are carefully neutralized with N sulphuric acid using phenolphthalein as indicator, and the chlorine is then determined with standard silver nitrate and potassium chromate.

To find the approximate amount of chloroform in a mixture, digest 1 c.c. for an hour with 25 c.c. N alcoholic potash and titrate the excess of alkali.

1 c.c. alkali consumed × 0·02977 = amount of chloroform per c.c.

Method of M. Nicloux ["Compt. rend.," 1906, 142, 163].

Small quantities of chloroform (0·004 to 0·1 gm.) can be estimated by heating for 1 hour in reflux apparatus 60 c.c. alcohol containing the chloroform, with 10 c.c. of a 10 per cent alcoholic potash solution, adding 15 c.c. of water to the cooled liquid, neutralizing in the presence of phenol phthalein and titrating the chlorine with $\frac{N}{20}$ $AgNO_3$ solution.

Method of M. Nicloux ["Bull. Soc. Chim.," 1906, (iii), 35, 321].

Estimation of Alcohol in Chloroform.—The alcohol is washed out by shaking 5 c.c. of the chloroform with 20 c.c. water, the latter being run off and the alcohol in it estimated colorimetrically with potassium dichromate.

Method of L. de St. Martin ["Compt. rend.," 106, 492].

A solution of alcoholic KOH decomposes chloroform slowly at the ordinary temperature, but the decomposition is rapid at 100°. If the strength of KOH is known, the excess may be titrated using phenolphthalein as indicator. After the liquid has cooled down, the amount of KCl formed may be estimated by silver nitrate.

In the cold solution, the alcohol and potassium formate have no effect on the titration.

It is best to heat with alcoholic potash in sealed tubes.

CHLORAL HYDRATE.

Titration.

Jules Garnier [Bull. Sci. Pharmacol., 1908, 15, 77].

In order to prevent a secondary reaction from taking place between the chloroform formed and the alkali the test is carried out as follows:—

0·1655 gm. of the sample is dissolved in 10 c.c. water and 12·5 c.c. $\frac{N}{10}$ KOH solution are added. The temperature should not exceed 15°, and after 15-20 minutes the excess of alkali is titrated with $\frac{N}{10}$ H_2SO_4 with phenolphthalein as indicator. A second experiment should be made using only the slightest excess of alkali.

See also T. E. Wallis ["Pharm. J.," 1906, 76, 162].

V. Meyer and H. Haffter ["Ber. vi," 600].

In this method, excess of normal alkali is added and the excess is back-titrated with standard acid.

It was found that $\frac{N}{10}$ soda did not decompose the chloral hydrate completely.

Estimation by Zinc.

P. A. W. Self ["Pharm. J.," 1907, (iv), 25, 4].

A weighed quantity of about 0·3 gm. chloral hydrate is boiled with 60 c.c. water and 2 gms. pure zinc dust for 20 minutes in a reflux apparatus. The condenser is washed with a little water and the solution is treated while hot with 10 c.c. acetic acid. After 2 minutes the solution is filtered, and the chlorine in the filtrate is estimated gravimetrically or volumetrically.

Iodometric Estimation.

Erwin Rupp ["Arch. Pharm.," 1903, 241, 326].

A one per cent solution of chloral hydrate is formed and 10 c.c. allowed to remain for 5 to 10 minutes in a stoppered bottle with a mixture of 25 c.c. $\frac{N}{10}$ iodine solution with 2·5 c.c. of N. potash solution. The solution is then diluted with 50 c.c. water, 5 c.c. HCl added, and the iodine liberated is titrated with $\frac{N}{10}$ thiosulphate solution.

$$CCl_3 . CHO, H_2O + I_2 + 2KOH = 2KI + 2H_2O + CO_2 + CHCl_3.$$

IODOFORM.

In general, methods for the determination of substances such as iodoform are based on the fact that the halogen may be fixed and hence estimated. The usual agent employed in this connexion is silver nitrate, but the subsequent determination differs in methods suggested by various investigators.

1. Excess of silver nitrate is titrated by Volhard's method.

Methods of E. H. Gane and W. H. Webster, M. Lehmann, and G. Frerichs.

2. The iodoform is hydrolysed and the alkaline halide titrated against silver nitrate.

Methods of H. D. Richmond, Gane and Webster.

3. Silver nitrate is added and the liberated nitric acid is titrated with alkali.

Method of Greshoff.

I.—Method of Gane and Webster ["Zeit. angew. Chem.," 1909, 22, 1059].

0·5 gm. of the sample is dissolved in 10 c.c. of a mixture composed of one part of ether to two parts of alcohol. To this are added 50 c.c. of deci-normal silver nitrate solution and then 1 c.c. of cold fuming nitric acid; the whole is then heated on a water bath until evolution of nitrogen oxides has ceased. The mixture is then diluted with 100 c.c. water and the excess of silver nitrate is determined with standard thiocyanate solution using ferric alum as indicator (Volhard).

The authors have proposed the following reaction for the estimation of *thymol iodide*.

Fuse together in a deep covered porcelain crucible, one gm. of the sample, 1 gm. of potassium sodium tartrate, and 5 gms. of dry sodium carbonate, the ingredients having been thoroughly mixed and covered with a layer of the soda mixture. The fusion is carried out gradually and should take about three quarters of an hour.

The melt is then extracted with water, and one-third of the filtrate is exactly neutralized with 5 per cent nitric acid using

methyl orange paper as an indicator. A trace of calcium carbonate is now added and the iodine estimated by standard silver nitrate using potassium chromate as indicator. The liquid is now acidified with nitric acid and the silver halide collected and weighed as usual. Should chloride be present, this weight of silver halide will not correspond to the titration number, but the exact amount of iodine present may be found by easy calculation.

Method of M. Lehmann ["Chem. Cent.," 1900, 19, 693].

For the estimation of iodoform in dressing materials, 10 gms. are treated with 100 gms. of "spiritus athereus" at 15° to 20° for thirty minutes in a stoppered bottle with frequent shaking. Ten gms. of the solution are mixed in an Erlenmeyer flask with fifteen to twenty drops of fuming nitric acid, and an excess of standard deci-normal silver nitrate added. The whole is then heated on a water bath until the silver halide has settled and the supernatant liquid is clear and colourless. After cooling, 125-140 c.c. of water are added and the excess of silver nitrate titrated with thiocyanate solution.

In a later paper Lehmann ["Pharm. Zeit.," 45, 522] has modified the above method by treating 10 gms. of the sample with 200 c.c. of the ether alcohol mixture for 24 hours at 20°-25°. Twenty c.c. of this solution are then treated as above.

Method of G. Frerichs ["Chem. Cent.," 1900 (ii), 785].

For the estimation of iodoform in dressing materials, 1-2 grms. are placed in an Erlenmeyer flask with 10-20 c.c. of alcohol. Excess of $\frac{N}{10}$ silver nitrate and 10 c.c. dilute nitric acid are added and the mixture left for a quarter of an hour. The excess of silver nitrate is then estimated as directed above.

II.—Method of H. D. Richmond [" Analyst," 17, 7].

Dissolve 0·15 gm. of sample in alcohol, add excess of alcoholic soda, and digest near the boiling-point for 10 minutes in a reflux apparatus. The excess of spirit is then distilled off and the residue taken up with water. The solution is slightly acidified with dilute nitric acid and then neutralized by a trace of calcium carbonate.

The alkaline halide solution is now titrated with a weak standard solution of silver nitrate using potassium chromate as indicator.

Method of Gane and Webster, [" Zeit. angew. Chem.," 1909, 1059].

In addition to the method described under heading I, the authors based a method on the saponification of the iodoform by prolonged boiling with strong alcoholic potassium hydroxide. The excess of alkali is neutralized with dilute nitric acid as in the above method and the potassium iodide titrated with silver nitrate solution.

The authors prefer the first method already described.

III.—Method of Greshoff [" Rec. trav. Chim.," 7, 342].

Iodoform is treated with silver nitrate solution at the ordinary temperature when the following reaction occurs :—

$$CHI_3 + 3AgNO_3 + H_2O = 3AgI + 3HNO_3 + CO$$

The reaction takes about an hour and a half for completion, and the nitric acid liberated is titrated with alkali.

The above method is not so practicable as those already described under headings I and II.

HYDROXYLAMINE.

Meyeringh ["Ber.," 1877, 10, 1940]; A. W. Stewart ["J.C.S.," 1905, 410].

Hydroxylamine is decomposed by warming with iodine solution and the hydriodic acid formed is taken up by sodium phosphate before it affects the oxime. The unchanged iodine is titrated against sodium thiosulphate.

The solution of hydroxylamine should be approximately $\frac{N}{12}$ $(NH_2OH)_2H_2SO_4$. Ten c.c. of this are mixed with 40 c.c. $\frac{N}{10}$ iodine solution and 20 c.c. $\frac{N}{5}$ disodium hydrogen phosphate solution added. The solution is gently warmed on water bath for a minute or so and the excess of iodine titrated with $\frac{N}{10}$ thiosulphate.

$$2NH_2OH + 2I_2 = N_2O + H_2O + 4HI.$$

Estimation of Hydroxylamine in Oximes and of Phenylhydrazine in Hydrazones and Osazones.

Siro Grimaldi ["Chem. Cent.," 1903 (i), 97, from "Staz. sperim. agrar. ital.," 35, 738].

The oxime, etc., is introduced into a flask with a long narrow neck and heated with 100 c.c. of standardized HCl for 1 hour on the water bath. The regenerated aldehyde or ketone is removed (and may be weighed as confirmatory data) and the excess of acid is titrated with say, $\frac{N}{100}$ NaOH solution.

From the amount of acid absorbed, the phenylhydrazine or hydroxylamine is calculated.

PHENYLHYDRAZINE.

Henri Causse ["Compt. rend.," 1897, 125, 712].

About 0·2 gm. phenylhydrazine, free or in combination, is mixed with excess of a solution prepared by dissolving 125 gms. arsenic acid in a mixture of 450 gms. of water and 150 gms. of concentrated HCl, filtering after cooling, and then diluting to 1000 c.c. with glacial acetic acid.

The mixture is gently heated and finally boiled in a reflux apparatus. After about 40 minutes the liquid is allowed to cool, made alkaline with NaOH solution, reacidified with HCl, mixed with excess of $NaHCO_3$ and titrated with $\frac{N}{10}$ iodine solution.

The method is applicable to combinations of phenylhydrazine with aldehydes. If the aldehyde is aromatic it has no influence on the result; fatty aldehydes must be removed.

198 gms. of arsenious acid are formed for every 108 gms. of phenylhydrazine oxidized.

BENZENOID QUINONES.

A. Valeur ["Bull. Soc. Chim.," 1900, 23, 58].

This method is based on the reaction expressed in the following equation:—

$$C_6H_4O_2 + 2HCl + 2KI = C_6H_6O_2 + 2KCl + I_2.$$

Dissolve sufficient quinone in 95 per cent alcohol to liberate 0·2-0·5 gm. iodine. Add to this a rapidly prepared mixture of 20 c.c. of a 10 per cent solution of potassium iodide with 20 c.c. hydrochloric acid previously diluted with an equal volume of 95 per cent alcohol and cooled.

The liberated iodine is titrated with standard sodium thiosulphate solution. It is necessary to mix the potassium iodide and hydrochloric acid as the acid would react with the quinone and the iodide would oxidize it.

Good results were obtained with toluquinone and thymoquinone.

ETHER.

Rosaniline acetate is insoluble in ether, but when alcohol or water is present it imparts a colour to the mixture.

Procedure devised by Allen ["Commercial Organic Analysis," Vol. I, p. 230].

A small quantity of rosaniline acetate is placed in a separator which is then filled with water and a small proportion of ether, and the whole agitated. A coloured etherized water is obtained, in which ether is quite insoluble, while alcohol readily dissolves; 10 c.c. of the etherized water are run into a glass tube holding about 25 c.c. and having divisions of 0·1 c.c.; 10 c.c. of the sample of ether are next added, the tube corked, and the whole well shaken. On the ether rising to the surface, its volume can be easily read off. Any reduction in its volume is due to admixture of alcohol. Each 0·1 c.c. lost represents 1 per cent of alcohol. If the alcohol does not exceed 20 per cent, the ether will be colourless and the result of the experiment is correct; but if the alcohol is much above 20 per cent, the ether will be coloured and the result below the truth. The absence of colour, therefore, in the ethereal layer, indicates the accuracy of the experiment. If the ether is coloured, an accurate result can still be obtained by adding 5 c.c. of anhydrous ether, and again agitating. It is better, however, to dilute a fresh portion of the sample with an equal bulk of pure ether, and use the diluted sample instead of the original. By proceeding in this manner the proportion of alcohol in mixtures of that liquid with ether can be ascertained within 1 or 2 per cent with great facility.

Paraffin in High Boiling-Point Petroleum.

D. Holde [" Chem. Rev. Fett. ü. Harz. Ind.," 4, 4, 21].

Ten to twenty c.c. of a sample solidifying at $-5°$ or 5 c.c. of a sample solidifying at 0° is dissolved in the smallest quantity of a mixture of ether and alcohol (1 : 1) in a 200 c.c. Erlenmeyer flask cooled to $-20°$ in a freezing mixture. More alcohol-ether is added until no more oil drops are visible and only a flocculent deposit of paraffin is apparent. The liquid is filtered in a funnel surrounded by ice-salt freezing mixture and washed with ether-alcohol cooled to $-20°$. If a hard paraffin is dealt with, a mixture of 1 volume ether and 1 volume of alcohol is used ; if a soft paraffin, 1 volume ether with 2 volumes of alcohol is used.

The insoluble residue is dissolved with hot benzene which is evaporated in a weighed beaker.

ACETYLENES.

R. Chavastelon [" Compt. rend.," 1896, 125, 245].

Acetylene reacts with excess of silver nitrate in water or alcohol according to :—

$$C_2H_2 + 3\ AgNO_3 = C_2Ag_2,\ AgNO_3 + 2HNO_3.$$

The author suggests this as a method by titrating the nitric acid produced. The gas must be free from acid vapours and the operation is best carried out in a Raoult absorption eudiometer. The method is general for RC : CH.

ANTHRACENE.

Henry Bassett ["Chem. News," 1896, 73, 178].

The sample is oxidized in the usual way using 15 gms. of chromic acid; after some hours it is diluted with 400 c.c. water and after 3 hours is filtered, washed with water, and dried in a water oven. The quinone is transferred to a flask with 45 c.c. glacial acetic acid, 2·5 c.c. chromic acid solution containing 1·5 gms. acid, and 10 c.c. nitric acid (sp. gr. 1·420) and boiled for an hour in a reflux apparatus. The following day it is diluted with 400 c.c. water and after 3 hours is filtered and washed successively with water, boiling 1 per cent alkali, and hot water.

The quinone is dried at 100°, heated for 10 minutes on a water bath with ten times its weight of pure, concentrated, hot, not fuming H_2SO_4, left during the night to absorb water in a covered tray of water, diluted, filtered, washed again with water, boiling alkali, and hot water, then dried, weighed, and calculated to anthracene.

ANALYSIS OF COMMERCIAL VINEGAR.

The Association of Official Agricultural Chemists has drawn up a scheme of analysis of this important technical product which is published in "Bull. 107 U.S. Bureau of Chemistry".

The full analysis consists of the following processes:—

(1) Microscopic examination of sediment.

(2) Alcohol, by distillation of the neutralized sample.

(3) Total solids.

(4) Ash.

(5) Examination of ash. Alkalinity and solubility. Phosphoric acid content.

(6) Total acids.

(7) Volatile acids by steam distillation.

(8) Fixed acids. Sulphuric and malic acids obtained by calculation from the results of (6) and (7).

(9) Potassium hydrogen tartrate.

(10) Tartaric acid by potassium acetate method.

(11) Mineral acids using litmus paper and methyl-violet. These are calculated as sulphuric acid.

ASSAY OF WOOD-NAPHTHA.[1]

Estimation of Methyl Alcohol.

The following modification of Krell's method is adopted in the British Government Laboratory :—

"Twenty-two gms. of coarsely-powdered iodine and 5 c.c. of distilled water are placed in a small flask and cooled by immersion in ice-cold water. Then 5 c.c. of the wood spirit (60·0° o.p.) are added, the flask corked, the contents gently shaken, and allowed to remain in the ice-cold bath for 10 to 15 minutes.

"When well cooled, 2 gms. of red phosphorus are added to the mixture of spirit and iodine in the flask, and the latter is immediately attached to a reflux condenser.

"The reaction soon commences, and must be moderated by dipping the flask into a cold water bath. (Spirit may be lost if the reaction is too violent.) After about 15 to 20 minutes, when all action appears to have ceased, the water bath under the flask is gradually heated to a temperature of about 75° (167° F.), and the flask being occasionally shaken is allowed to remain at this temperature for 15 to 20 minutes. The source of heat is then removed and the apparatus left for 1 hour till it has cooled, when the condenser is reversed, and the methyl iodide slowly distilled off—first at a low temperature—the bath being allowed to boil towards the end of the operation only. The end of the condenser dips into water in a measuring tube, and the iodide is collected under water and measured at a temperature of 60° F.

"The percentage by volume is found by the formula :—

$$\frac{\text{c.c. methyl iodide found} \times 0{\cdot}647 \times 100}{\text{c.c. wood spirit taken}} = \text{percentage of methyl alcohol.}$$

Or when 5 c.c. of spirit are taken,

c.c. methyl iodide × 12·94 = percentage by volume."

It should contain at least 72 per cent by volume.

[1] Reproduced, by special permission, from Allen's "Commercial Organic Analysis," Vol. I, Fourth Edition.

"Esters and acetals also yield methyl iodide by this process, and from the percentage of methyl alcohol calculated as above, an amount equivalent to the percentage of these substances present must be deducted. Practically, however, methyl acetate is the only compound usually found in quantity sufficient to materially affect the result. The number of gms. of methyl acetate per 100 c.c. of spirit multiplied by 0·5405 gives the equivalent of methyl alcohol to be deducted from the total percentage by volume calculated from the methyl iodide found."

The alcohols can be separated from the secondary constituents of wood-spirit by shaking with light petroleum and saturated brine. The saline layer is then distilled and the alcohols in the distillate determined by the method of Thorpe and Holmes.

Estimation of Acetone and Higher Ketones.

Messinger's method ["Ber.," 1888, 21, 3366] is followed with but slight modification in the British Government Laboratory, where the following procedure is adopted.

"Twenty-five c.c. of $\frac{N}{1}$ sodium hydroxide are placed in a stoppered flask of about 200 c.c. capacity. To this is added 0·5 c.c. of the naphtha. The mixture is well shaken and allowed to stand 5 to 10 minutes. Into it from a burette $\frac{N}{5}$ iodine solution is run slowly, drop by drop, vigorously shaking all the time, till the upper portion of the solution, on standing a minute, becomes quite clear. A few c.c. more of $\frac{N}{5}$ iodine solution are added, as to get concordant results an excess of at least 25 per cent of the iodine required must be added. After shaking, the mixture is allowed to stand for 10 to 15 minutes, and then 25 c.c. $\frac{N}{1}$ sulphuric acid are added. The excess of iodine is liberated, titrated with $\frac{N}{10}$ sodium thiosulphate solu-

tion and starch, and half the number of c.c. of thiosulphate solution used are deducted from the total number of c.c. of iodine solution used. The difference gives the amount of acetone by weight in the naphtha by the formula : c.c. $\frac{N}{5}$ iodine solution required × 0·387 = gm. of acetone per 100 c.c. of wood naphtha.

" This includes as acetone any aldehydes, etc., capable of yielding iodoform by this reaction.

" If the quantity of ' acetone ' is excessive, a less quantity of the spirit is taken, or 10 c.c. are diluted with 10 c.c. of methyl alcohol free from acetone, and 0·5 c.c. of the mixture is used."

Messinger in his original communication calls attention to the fact that commercial sodium hydroxide may contain nitrite, which must be allowed for. This is easily done by adding a crystal of potassium iodide to 25 c.c. of the $\frac{N}{1}$ sodium hydroxide, acidifying and titrating against the standard thiosulphate. Pure sodium hydroxide may be obtained with little difficulty.

One hundred c.c. of spirit should contain not more than 12 gms. of ketones, etc., as " acetone ".

Estimation of Esters.

In the British Government Laboratory, the hydrolysis of esters is conveniently effected in a silver pressure flask of about 150 c.c. capacity.

To 5 c.c. of the naphtha contained in a small Jena glass flask, 20 c.c. of recently boiled distilled water are added, and then 10 c.c. of $\frac{N}{1}$ sodium hydroxide and the whole heated for 2 hours under a reflux condenser on the water bath. The liquid is then cooled, phenolphthalein added, and the excess of sodium hydroxide titrated with $\frac{N}{1}$ acid.

Let the amount of acid required be x c.c. Then the number of gms. of esters (calculated as methyl acetate) in

100 c.c. of the sample is 1·48 (10 − x). If the proportion of esters is very small, and it is required to estimate them with great accuracy, a much larger quantity of spirit may be taken, and $\frac{N}{10}$ alkali and acid used, but in this case the spirit should be first boiled under a reflux condenser to expel carbon-dioxide. Wood spirit is generally almost neutral to phenolphthalein, but if not it must of course be rendered neutral before proceeding to the estimation of esters; 100 c.c. should contain not more than 3 gms. of esters.

Bromine Test for Unsaturated Compounds.

No accurate method for the estimation of allyl alcohol in wood naphtha exists, but the amount of bromine which the naphtha will decolorize is some measure of the unsaturated compounds, of which allyl alcohol is known to be one commonly present.

A standard bromine solution is made by dissolving 12·406 gms. of potassium bromide and 3·481 gms. of potassium bromate in a litre of recently boiled distilled water.

Fifty c.c. of this standard solution (= 0·5 gm. bromine) are placed in a flask of about 200 c.c. capacity, having a well-ground stopper. To this is added 10 c.c. of dilute sulphuric acid (1 in 4) and the whole shaken gently. After standing for a few minutes the wood naphtha is slowly run in from a burette into the clear brown solution of bromine until the latter is completely decolorized. Not more than 30 c.c. should be required.

Estimation of Basic Substances.

These (pyridines, mono-, di-, and tri-methylamine) can be to some extent measured by the methyl orange alkalinity of the sample, though as it is not known which base predominates, it is not usual to calculate the bases, as pyridine for instance, in the manner in which the ketones are calculated as acetone and the esters as methyl acetate.

For use as a denaturant in Britain, wood naphtha must comply with the following specification as to reaction with indicators :—

"The naphtha should be faintly acid to phenolphthalein, slightly alkaline or neutral, barely acid to litmus, and always alkaline to methyl orange. Twenty-five c.c. of the wood naphtha are placed in each of two beakers, and titrated with $\frac{N}{10}$ acid, using in one case a few drops of litmus solution, and in the other of a solution of methyl orange as indicator. With litmus usually 0·1 to 0·2 c.c. of $\frac{N}{10}$ acid is required to neutralize. With methyl orange the total alkalinity should be greater, at least 5 or 6 c.c. of $\frac{N}{10}$ acid being required for neutralization.

"The total alkalinity, less that given by litmus, is the 'methyl orange alkalinity' and, for the 25 c.c. of wood spirit, should not be less than is required to neutralize 5 c.c. of $\frac{N}{10}$ acid."

NAME INDEX.

Adam, 90.
Allen, 61, 149, 159, 240, 268.
Allihn, 152, 155, 165.
Apitzsch, 58.
Argenson, 199, 200.
Arnold, 48.
Asboth, 48.
Auld, 255.
Austin, 67.

Bacon, 55.
Bader, 209.
Bardin, 245.
Bassett, 270.
Bates, 142.
Baubigny, 57.
Baxter, 233.
Bay, 59, 64.
Bayliss, 62.
Beckmann, 14, 20.
Béhal, 229.
Bekk, 39.
Benedict, 199, 201, 202, 205.
Bennett, 247.
Berry, 55.
Bertrand, 124, 156, 157.
Blackadder, 39.
Blake, 142.
Blank, 193, 196.
Bleier, 7.
Blount, 40, 218.
Bloxam, 176.
Böddener, 163.
Bölsing, 90.
Bondi, 207.
Bordas, 239.
Boswell, 40, 41.
Bougault, 238.
Breteau, 40.
Brock, 214.
Brown, 165, 166.
Browne, 140, 147, 159.
Browning, 65, 66.
Budai, 258.
Bülow, 234.
Busch, 101.

Cahen, 65.
Cameron, 232.
Cantor, 202, 205.
Carius, 50, 53, 57, 58, 59, 61, 62.
Carr, 45.
Causse, 267.
Cedivoda, 213.
Chandelon, 207.
Chandelot, 212, 213.
Chavastelon, 269.
Christensen, 190.
Clerget, 143.
Conradson, 61.
Cook, 100.
Crace-Calvert, 174.
Craig, 242.
Crossley, 178.

Davis, 161.
Dehn, 164.
Decker, 101.
De la Harpe, 109, 111.
Denigès, 251.
Dennstedt, 31, 32, 34, 39, 40.
De Ste. Martin, 260.
Ditz, 213.
Dobriner, 257.
Dodge, 247.
Duclaux, 199, 200.
Dumas, 9, 42, 45.
Dunning, 244.
Dunstan, 45.
Durien, 221.
Dyer, 49.

Edinger, 58.
Edwards, 80.
Effront, 84.
Eschka, 60.

Fanto, 202, 205.
Feder, 235.
Fehling, 121, 124, 145.
Feinberg, 127, 247, 249.
Finkenbeiner, 193, 196.
Fischer, 193, 196.

François, 256.
Frerichs, 263, 264.
Fresenius, 236.
Freyer, 229, 237.
Fritzsche, 174.
Fuchs, 77, 79.

Gane, 263, 265.
Garnier, 261.
Gay Lussac, 200.
Giacosa, 207.
Gibello, 245.
Giraud, 111.
Goldschmiedt, 75, 101.
Gooch, 65, 66.
Gräfe, 61.
Gray, 40, 45.
Green, 113, 117.
Greshoff, 263, 265.
Grignard, 92, 106, 107.
Grimaldi, 266.
Groves, 42.
Grünhilt, 201.
Gunning, 49.

Haas, 45.
Haberland, 220.
Haffter, 261.
Hanus, 130, 249.
Hartmann, 89, 164.
Hehner, 193, 195, 202, 203, 204, 206.
Hemmelmayr, 75.
Hempel, 61.
Hérissey, 248.
Herzfeld, 143.
Herzig, 101.
Hesse, 190.
Hewitt, 93, 96.
Hibbert, 92, 106, 107, 114, 115.
Hofmann, 10.
Holde, 269.
Holmes, 193, 199, 273.
Hönigschmid, 101.
Hübl, 179, 180, 181, 183.
Hudson, 144.
Hunter, 80.

Jaffé, 202, 204.
Jean, 231, 233.
Johnson, 60.
Jolles, 251.
Jones, 225.
Joulin, 239.
Julius, 256.

Kaufler, 99.
Kebler, 254.
Kinnicut, 113.
Kippenberger, 188, 242.
Kjeldahl, 46, 48, 49, 84.
Klemenc, 102.
Knapp, 158.
Knecht, 114, 115, 167, 168.
Kohn, 7.
Koppeschaar, 207, 237.
Kossler, 207.
Köttstorfer, 184.
Krell, 272.
Kröber, 162, 163.
Krüger, 49.
Küster, 216.
Kux, 73.

La Coste, 65.
Lam, 193, 196.
Landolt, 207.
Landsberger, 15.
Larsen, 129.
Laurent, 136.
Legler, 242.
Lehmann, 263, 264.
Lerona, 40.
Leuchs, 176.
Lewkowitsch, 183, 185, 186, 187.
Leys, 226.
Liebig, 25.
Limpricht, 116.
Ling, 161.
Linneman, 57.
Lippich, 136.
Little, 65.
Lungwitz, 182.
Lutz, 84.

Marck, 39.
Marie, 64.
Marriott, 253.
Mathewson, 57.
Maumené, 177, 199, 200.
McEwan, 232.
McIlhiney, 82, 180, 187.
McLean, 124.
Meissl, 177, 186.
Messinger, 208, 236, 252, 273, 274.
Messner, 189.
Meyer, 5, 80, 89, 101, 108, 119, 261.
Meyeringh, 127, 266.
Michaelis, 65.
Micko, 239.
Millar, 166.
Mohr, 176.
Monthulé, 65.
Moore, 96.
Morgan, 65, 100.
Morris, 166.
Morse, 40.
Müller, 168, 172.

Nef, 113.
Neumann, 62, 63.
Nicloux, 259, 260.
Nicol, 135, 136.
Norris, 199, 201.

O'Sullivan, 144.
Oudemans, 190.

Paessler, 231.
Paterson, 17.
Pavy, 150.
Pellet, 142, 233.
Pence, 211.
Penny, 207.
Perkin, 85, 97.
Personne, 227.
Peška, 242, 243.
Petrenko-Kritschenko, 127.
Pflüger, 154.
Piria, 54.
Plimmer, 62.
Portès, 227.
Pringsheim, 56, 65.
Prunier, 199, 202.
Puckner, 259.

Raczkowski, 239.
Rawson, 171, 172, 174, 175.
Rebière, 222.
Redman, 214.
Reed, 222.
Regnault, 46.
Reichert, 177, 186.
Reid, 84.
Reinhardt, 257.
Reinige, 57.
Remsen, 84.
Renouf, 178.
Reverdin, 109, 111.
Richardson, 202, 204.
Richmond, 263, 265.
Rideal, 113.
Riegler, 215.
Ripper, 118, 128.
Rivals, 57.
Robertson, 61.
Robineau, 253, 254.
Rocques, 245.
Rollin, 253, 254.
Romijn, 243.
Röse, 199, 201.
Rother, 119.
Rupp, 225, 228, 262.
Russ, 129.
Ruyssen, 227.

Sachs, 142.
Sachsse, 158, 159, 165.
Saupe, 236.
Sawyer, 142.
Scala, 227.
Schaap, 224.
Scheuer, 253.
Schiff, 42, 54.
Schranz, 257.
Schrönrock, 139.
Schryver, 209.
Schulze, 104, 206.
Schweitzer, 182.
Seeker, 57.
Self, 261.
Seubert, 207.
Seward, 218.
Seyewetz, 129, 245.
Silvermann, 250.
Simpson, 42.
Sisley, 170.
Smith, 121, 125, 243.
Soleil, 139.
Sonnerschein, 217.
Soxhlet, 63, 158, 160.
Sparre, 227.
Stepanow, 54, 55.
Stewart, 127, 266.
Stillwell, 219.
Strache, 125.
Stritar, 193, 197.
Sudborough, 89, 92, 106.

Tempany, 142.
Tennant, 174.
Thomas, 89.
Thorpe, 193, 199, 200, 273.
Titherley, 209.
Tocher, 211.
Tollens, 162, 163, 164.
Tolmon, 144.
Tompson, 144.
Toth, 207.
Trillat, 241.
Tucker, 40.

Ullgreen, 172, 176.

Valeur, 267.
Van de Vyvere, 193, 199.
Van Slyke, 109.
Varrentrapp, 49, 91.
Vaubel, 112, 253.
Ventzke, 139, 147.
Verley, 90.
Volhard, 55, 56, 154, 244, 263.
Vortmann, 208, 236.

Wahl, 117.
Walker, 15, 29, 39.
Wallis, 261.

Warrington, 42, 48.
Washburn, 67.
Watts, 142.
Webster, 263, 265.
Wein, 159, 160.
Weinreb, 207.
Weith, 214.
Wellman, 249.
Wenzel, 87.
Wiechmann, 151, 157.
Wij, 181.
Will, 49.
Winton, 250.
Witt, 168.
Witz, 217.

Zanetti, 233.
Zeidler, 193, 197.
Zeisel, 93, 94, 97, 99, 100, 101, 193, 197, 198, 202, 205.
Zerewitinoff, 107.
Zimmermann, 213.

SUBJECT INDEX.

Acetaldehyde, 245.
Acetic acid, 217.
— separation from formic, butyric, and propionic, 220.
Acetone, 251, 273.
Acetyl value of fats, 185.
— method for glycerol, 205.
— group, 85 *et seq.*
Acetylation of amino-group, 111.
Acetylenes, 269.
Acid value of fats and oils, 184.
Acids, estimation, 217.
— iodine oxygen method, 73.
— carbonate method, 75.
— ammonia method, 82.
— H_2S method, 77.
Alcohols, 193 *et seq.*, 260.
Aldehydes, 118, 241.
Alkali metals in ultimate analysis, 31.
Alkaloids, 188 *et seq.*
Allihn's method, 152.
Allyl alcohol in naphtha, 275.
Amido-group, 84.
Amines—molecular weight, 104.
— fatty, 108.
— primary, 107, 113.
— secondary, 106.
Amino-group, 104.
Aniline, 256.
Anisic aldehyde, 130.
Anthracene, 270.
Antimony, 67.
Arsenic, 65.
Azo-dyes, 168 *et seq.*

Barley, starch in, 165.
Baryta solution, 72.
Basicity of acids, 72.
Basic compounds in naphtha, 276.
Beet leaves, oxalic acid in, 234.
Benzaldehyde, 129, 247.
Benzoic acid, 222.
— separation from salicylic, 224.
Benzopurpurin 4B, 170.
Bertrand's method, 156.
Bisulphite method for acetaldehyde, 128, 245.
— for benzaldehyde, 128.
Boiling-point, elevation of, 12.
Bromination of phenols, 207, 214.
Bromine, action on oils of, 178, 182.

Calcium formate and acetate, 229.
Cane sugar, 146, 149, 159.
Carbohydrates, 135.
Carbon, 25 *et seq.*
Carbon bisulphide in benzol, 60.
Carbonyl group, 118 *et seq.*
Carboxyl group, 71.
Catalytic decomposition, 31.
Cerium dioxide as catalyst, 39.
Chemical methods of sugar analysis, 145.
Chloral hydrate, 261.
Chloroform, 259.
Cinnamic acid, 238.
Clarification of sugars, 141, 143.
Colorimetric methods for alcohols, 200.
— carbohydrates, 164.
Commercial vinegar assay, 271.
Cresols, estimation of, 213.
Crystal scarlet 6R, 169.

Decolorization of inverted sugar solutions, 144.
Dextrose, estimation of, 148, 152, 161.
Double polarization, 143.
Dyestuffs, estimation of, 167.

Electrical methods for carbon, 40.
Esters, 83, 274.
Ether, 268.
Ethoxyl-group, 93 *et seq.*
Ethyl alcohol, 199.
— and methyl alcohol, 199, 202.

Fats, 177.
Formaldehyde, 129, 241.
Formate from acetate, separation of, 226, 229.

Formic acid, 225.
Fehling's solution, 121, 124, 145.
Freezing-point, lowering of, 19.
Furfural, 163.

Galactose, 148, 149.
Glucose (see Dextrose).
Glycerol, 202.
Glycogen, 162.
Grignard reagent, 92, 106.

Halogens, estimation of, 36, 50 *et seq.*
Hübl's method, 179.
Hydrazones of ketones, 130.
Hydriodic acid, preparation, 93.
Hydrogen, estimation of, 25 *et seq.*
Hydroxylamine, 266.
Hydroxyl group, 90.
Hydroxy-benzaldehyde, 130.

Imino-group, 104.
Indigo, 171 *et seq.*
Invert sugar, 157.
Iodine, derivatives of phenols, 208.
— estimation of, 57.
— monochloride, 181.
— values of fats, 179, 183.
Iodoform, 263.

Ketones, 118 *et seq.*, 273.

Lactic acid, 231.
Lactose, 157, 160, 161.
Levulose, 148, 149, 151.

Malonic acid, 232.
Maltose, 147, 149, 159, 160.
Methoxyl-group, 93 *et seq.*
— in sulphur compounds, 99.
Methyl alcohol, 193.
— in formaldehyde, 196, 197.
Molecular weight of acid, 71.
— base, 104.
— by physical methods, 5 *et seq.*

β-naphthol, 208, 216.
Neutral sulphite method for aldehydes, 129, 245.
Nitraniline, 167.
Nitriles, 85.
Nitrobenzene, 167.
Nitro-compounds, 167.
Nitro-group, 114.
Nitrogen, 42 *et seq.*
Nitrogen attached to methoxyl, 101.
Nitroso dimethylaniline, 167.
Nitroso-group, 115.

Objections to Hübl's method, 180.
Oils, 177 *et seq.*
Osmotic determination of molecular weight, 12.
Oxalic acid, 233.
Oxygen, estimation of, 40.

Paraffin in petroleum, 269.
Pavy solution, 150.
Pentosan, 163.
Pentoses, 162 *et seq.*
Phenols, 207, 208.
Phenylhydrazine, 266, 267.
— standardization of, 120, 124.
Phosphorus, 62.
Physical methods of determination of alcohol, 200.
Picric acid, 167, 235.
Polarimeters, 135.
Polarization by double refraction, 135.
— of raw sugars, 141.
Preparation of hypobromite, 212.
— — hypochlorite, 253.
— — hyposulphite, 172.
— — phloroglucinol, 164.
— — titanous chloride, 114.
Pyruric acid, 124.

Quinones, 267.

"R"-Salt, preparation and standardization of, 109.
Reichert-Meissl value of oil, 186.

Saccharimeters, 139.
Salicylaldehyde, 128, 131.
Salicylic acid, 209, 236.
Saponification of discoloured fats, 187.
— value of oils, 184.
Secondary amines (see Amines).
Silver nitrate, alcoholic, 94.
Sodamide, estimation of phenols by, 209.
Sodium nitrite, standardization of, 113.
Starch, 165.
Sublimation of indigo, 174.
Succinic acid, 239.
Sucrose (see Cane Sugar).
Sulphur, estimation of, 37, 53, 58.
— — in benzol, 60.
— — in coal, 60.
— — in fuels (review), 61.

Tartaric acid, 240.
Thiocyanate method for estimation of copper, 154.
Thymol, 208.
— iodide, 263.
Toluidine, 257.
Trimethylamine, 258.

Unsaturated compounds in wood naphtha, 275.
Unsaturation, 178.
Urea, 85.

Vanillin, 249.
Vapour densities, 5 *et seq.*
— pressure of water, 46.
Ventzke scale, 139.
Vinegar, acetic acid in, 221, 271.
— assay of commercial, 271.

Waxes (see Oils).
Wij's method, 181.
Wood naphtha, assay of, 196, 197, 272.

Zinc dust, valuation of, 117.

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